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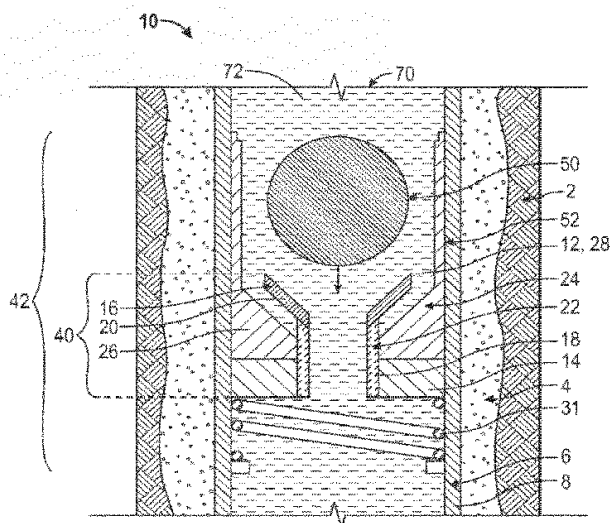

FIG. 1A

(57) Abstract: A selectively corrodible downhole article includes a movable cylindrical member comprising a first section and an axially separated second section, the first section comprising a first material having a first galvanic activity, the second section comprising a second material having a second galvanic activity, the first galvanic activity being greater than the second, the first section being electrically isolated from the second section; and a fixed member disposed on the cylindrical member and configured for electrical contact with the first or second section, the fixed member comprising an intermediate material having an intermediate galvanic activity, the intermediate galvanic activity being intermediate the first and second galvanic activity., the movable cylindrical member configured for movement from a first position where the first section is disposed and in electrical contact with the fixed member and a second position where the second section is disposed and in electrical contact with the fixed member.

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SELECTIVELY CORRODIBLE DOWNHOLE ARTICLE AND METHOD OF USE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Application No. 13/371788, filed on February 13, 2012, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] Certain downhole operations involve placement of elements in a downhole environment, where the element performs its function, and is then removed. For example, elements such as ball/ball seat assemblies and fracture (frac) plugs are downhole elements used to seal off lower zones in a borehole in order to carry out a hydraulic fracturing process (also referred to in the art as "fracking") to break up different zones of reservoir rock. After the fracking operation, the ball/ball seat or plugs are then removed to allow, *inter alia*, fluid flow to or from the fractured rock.

[0003] Balls and/or ball seats, and frac plugs, can be formed of a corrodible material so that they need not be physically removed intact from the downhole environment. In this way, when the operation involving the ball/ball seat or frac plug is completed, the ball, ball seat, and/or frac plug is dissolved away. Otherwise, the downhole article may have to remain in the hole for a longer period than is necessary for the operation.

[0004] To facilitate removal, such elements can be formed of a material that reacts with the ambient downhole environment so that they need not be physically removed by, for example, a mechanical operation, but instead corrode or dissolve in the downhole environment. In order to employ dissolution or corrosion to remove downhole elements, it is very desirable to develop downhole articles and methods of their use whereby the dissolution or corrosion and removal of these elements may be selectively controlled.

SUMMARY

[0005] In an exemplary embodiment, a selectively corrodible downhole article is disclosed. The article includes a movable cylindrical member comprising a first section and an axially separated second section, the first section comprising a first material having a first galvanic activity, the second section comprising a second material having a second galvanic activity, the first galvanic activity being greater than the second galvanic activity, the first section being electrically isolated from the second section. The article also includes a fixed member disposed on the cylindrical member and configured for electrical contact with the

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first section or the second section, the fixed member comprising an intermediate material having an intermediate galvanic activity, the intermediate galvanic activity being intermediate the first galvanic activity and the second galvanic activity, the movable cylindrical member configured for movement from a first position where the first section is disposed on and in electrical contact with the fixed member and a second position where the second section is disposed on and in electrical contact with the fixed member, wherein in the first position, the first section is configured for selective dissolution, and wherein in the second position, the fixed member is configured for selective dissolution.

[0006] In another exemplary embodiment, a method of removing a selectively corrodible downhole article is disclosed. The method includes disposing downhole a selectively corrodible downhole article, comprising: a movable cylindrical member comprising a first section and an axially separated second section, the first section comprising a first material having a first galvanic activity, the second section comprising a second material having a second galvanic activity, the first galvanic activity being greater than the second galvanic activity, the first section being electrically isolated from the second section; and a fixed member disposed on the cylindrical member and configured for electrical contact with the first section or the second section, the fixed member comprising an intermediate material having an intermediate galvanic activity, the intermediate galvanic activity being intermediate the first galvanic activity and the second galvanic activity, the movable cylindrical member configured for movement from a first position where the first section is disposed on and in electrical contact with the fixed member and a second position where the second section is disposed on and in electrical contact with the fixed member, wherein in the first position, the first section is configured for selective dissolution, and wherein in the second position, the fixed member is configured for selective dissolution. The method also includes exposing the selectively corrodible downhole article to a first wellbore fluid while the movable cylindrical member is in the first position, wherein the first section is selectively dissolved. The method further includes moving the movable cylindrical member to the second position and exposing the selectively corrodible metallic downhole article to a second wellbore fluid, wherein the fixed member is selectively dissolved.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Referring now to the drawings wherein like elements are numbered alike in the several Figures:

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[0008] FIG. 1A is a cross-sectional view of an exemplary embodiment of a selectively corrodible downhole article comprising a ball, ball seat and movable cylindrical sleeve in a first position as disclosed herein;

[0009] FIG. 1B is a cross-sectional view of the exemplary embodiment of a selectively corrodible downhole article of FIG. 1A with the movable cylindrical sleeve in a second position as disclosed herein;

[0010] FIG. 2A is a cross-sectional view of an exemplary embodiment of a selectively corrodible downhole article comprising a plug, plug seat and movable tubular article in a first position as disclosed herein;

[0011] FIG. 2B is a cross-sectional view of the exemplary embodiment of a selectively corrodible downhole article of FIG. 2A with the movable tubular article in a second position as disclosed herein; and

[0012] FIG. 3 is a flowchart of an exemplary embodiment of a method of removing a selectively corrodible downhole article.

DETAILED DESCRIPTION OF THE INVENTION

[0013] Referring to the figures, and particularly FIGS. 1-3, a method 100 of removing a selectively corrodible downhole article 10 from a wellbore 70 is disclosed. The wellbore 70 may be formed in an earth formation 2 and may include a cement casing 4. The wellbore may also include a liner 6, which may include a plurality of metal tubulars (tubular sections) 8. The selectively corrodible downhole article 10 may comprise any suitable downhole article, including various downhole tools or components. In one embodiment, the selectively corrodible downhole article 10 may include a selectively corrodible ball 50 and ball seat 52, such as a frac ball and complementary ball seat, or a selectively corrodible plug 60 and plug seat 62, such as a frac plug and complementary plug seat. The article 10 is configured for selective dissolution in a suitable wellbore fluid 72, 74 acting as an electrolyte.

[0014] The article 10 includes a movable member, such as a movable cylindrical member 12, comprising a first section 14 and an axially separated second section 16. The first section 14 comprising a first material 18 having a first galvanic activity. The second section 16 includes a second material 20 having a second galvanic activity. The first galvanic activity is greater than the second galvanic activity, such that it has a greater tendency to corrode in a given wellbore fluid as an electrolyte. The first section 14 is electrically isolated from the second section 16. Electrical isolation may be accomplished by any suitable electrical isolator 22. A suitable electrical isolator may include any suitable electrically

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insulating material, particularly an electrically insulating polymer or ceramic, or a combination thereof.

[0015] The article 10 also includes a fixed member 24 disposed on the movable cylindrical member 12 or movable cylindrical member 12 may be disposed within fixed member 24. The movable cylindrical member 12 and fixed member 24 are both electrically conductive. The fixed member 24 is configured for electrical contact with the first section 14 or the second section 16, the fixed member 24 comprising an intermediate material 26 having an intermediate galvanic activity, the intermediate galvanic activity being intermediate the first galvanic activity and the second galvanic activity. The movable cylindrical member 12 is configured for movement from a first position 28 where the first section 14 is disposed on and in electrical contact with the fixed member 24 and a second position 30 where the second section 16 is disposed on and in electrical contact with the fixed member 24. In the first position 28, the first section 14 is configured for selective dissolution because the first material 18 is more galvanically active (i.e., is more reactive) than the intermediate material 26. In the second position, the fixed member 24 is configured for selective dissolution because the intermediate material 26 is more galvanically active than the second material 20. The first material 18, intermediate material 26 and second material 20 may each be, for example, a different metal from the galvanic series having the relative activities described herein. The first material 18, intermediate material 26 and second material 20 contact each other as described herein in the presence of a wellbore fluid that comprises an electrolyte, such as for example a brine, acidizing fluid, drilling mud or the like.

[0016] Referring to FIGS. 1A and 1B, the selectively corrodible article 10 may include a ball 50 and ball seat 52. In one embodiment, at least one of ball 50 and ball seat 52 comprise intermediate material 26. In this embodiment, while at least one of ball 50 and ball seat 52 comprise intermediate material 26, the other of the ball 50 and ball seat 52 may include another electrically conductive material that is less galvanically active than the material intermediate material 26. For example, the ball 50 may be formed from intermediate material, and the ball seat may be formed from a less galvanically active material, such that the ball 50 is configured for removal as described herein. Alternately, the ball seat 52 may be formed from intermediate material, and the ball may be formed from a less galvanically active material, such that the ball seat 52 is configured for removal from the wellbore 70 as described herein, and the ball 50 may be allowed to fall to a lower portion of the wellbore 70. In another embodiment, both the ball 50 and ball seat 52 may comprise intermediate material 26 and are configured for removal from the wellbore 70 as described herein.

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[0017] Referring to FIGS. 2A and 2B, the selectively corrodible article 10 may include a plug 60, such as a frac plug, or a plug seat 62. In one embodiment, at least one of plug 60 and plug seat 62 comprise intermediate material 26. In this embodiment, while at least one of plug 60 and plug seat 62 comprise intermediate material 26, the other of the plug or plug seat 62 may include another electrically conductive material that is less galvanically active than the material intermediate material 26. For example, the plug 60 may be formed from intermediate material, and the plug seat 62 may be formed from a less galvanically active material, such that the plug 60 is configured for removal as described herein. Alternately, the plug seat 62 may be formed from intermediate material, and the plug 60 may be formed from a less galvanically active material, such that the plug seat 62 is configured for removal from the wellbore 70 as described herein, and the plug 60 may be allowed to fall to a lower portion of the wellbore 70. In another embodiment, both the plug 60 and plug seat 62 may comprise intermediate material 26 and are configured for removal from the wellbore 70 as described herein.

[0018] Referring to FIGS. 1A and 1B, in one embodiment the movable cylindrical member 12 may include a slidable sleeve 40 disposed within a tubular article 42 that may be moved axially upwardly or downwardly within the wellbore 70. In another embodiment, the movable cylindrical member 12 may include a movable tubular article 44 that may be moved axially upwardly or downwardly within the wellbore 70, as illustrated in FIGS. 2A and 2B. While the movable cylindrical member 12 is illustrated in FIGS. 2A and 2B with the first section 14 uphole (closer to the surface) from the second section 16 (FIG. 2A), such that the movable member 12 is moved uphole (FIGS. 1B and 2B) in accordance with method 100, as described herein, it will be understood that the positions of the first section 14 and the second section 16 may be reversed, such that the first section 14 is downhole (farther from the surface) from the second section 16, such that the movable member 12 is moved downhole in accordance with method 100, as described herein and illustrated in FIGS. 1A and 1B.

[0019] Referring to FIGS. 1A and 1B, in one embodiment the slidable sleeve 40 includes a first section 14 having a shape, such as the shape of a cylindrical ring or hollow cylinder, which is configured to abut the lower surface of the ball seat 52 in intimate touching contact sufficient to establish electrical contact between them for the purposes described herein. First section 14 formed from first material 18 is attached proximate a lower end of an electrical isolator 22 that may have any suitable shape, such as a hollow cylindrical shape, and is slidably disposed within the central bore of ball seat 52 and configured to move from first position 28 (FIG. 1A) to second position 30 (FIG. 1B). Slidable sleeve 40 also includes

a second section 16 having a shape, such as the shape of a hollow frustoconical disk, which is configured to sealing engage the upper seating surface of the ball seat 52 in intimate touching and sealing contact sufficient to establish electrical contact and sealing contact between them for the purposes described herein. Second section 16 formed from second material 20 is attached proximate an upper end of the electrical isolator 22. In the first position 28, the second section 16 is electrically isolated from the ball seat 52 in the presence of first wellbore fluid 72 that is configured to act as an electrolyte and first section 14 is in electrical contact with the ball seat. As described herein, the first material 18 is configured to be more galvanically active in the electrolyte than the intermediate material 26 of the ball seat 52, such that the ball seat is protected from corrosion in first position 28, and first material is configured to be selectively corroded or dissolved in the first fluid 72. First position 28 may, for example, represent preparation and configuration of a section of the wellbore for a completion operation. The first section 14 may be biased against the ball seat 52 by a bias member, such as, for example, bias spring 31. Bias spring 31 may be configured for eventual removal by an appropriate wellbore fluid, such as second wellbore fluid 74, or may be configured such that its presence in the wellbore does not substantially interfere with the intended wellbore operations. Once the wellbore has been configured, it may be desirable to perform an operation such as fracturing by insertion of a ball 50 in first wellbore fluid 72 (FIG. 1A) and pressurization of a second wellbore fluid 74 that is also configured to act as an electrolyte as shown in FIG. 1B. Pressurization of the second fluid 74 drives the ball 50 into the second section 16 thereby causing the slidable sleeve 40 to slide to second position 30 where the second section is in intimate electrical contact with the surface of ball seat 52 such that the wellbore operation may be performed in the pressurized portion of the wellbore above the seal formed between ball 50, second section 16 and ball seat 52. The first section 14 moves out of electrical contact with the ball seat 52 and ceases to provide galvanic protection afforded in the first position 28. In the second position 30, the intermediate material of the ball seat 52 and/or ball 50, for example, is more galvanically active than the second material 20 of the second section 16, thereby causing the ball seat 52 and/or ball 50 to corrode or dissolve in preparation for its eventual removal from the wellbore. The absolute and relative galvanic activity of intermediate material 26 and second material 20 may be selected to establish a predetermined time interval for performing the desired wellbore operation such as fracturing, including a predetermined interval for removal of the ball seat 52 and/or ball 50, as described herein. Since the ball seat 52 is supporting the ball 50 and slidable sleeve 40, it will be understood that its corrosion or dissolution will cause the ball 50

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and slidable sleeve 40 to be removed from the location shown in the wellbore, such as by falling to a lower portion of the wellbore, such as the bottom of the wellbore.

[0020] The first material 18 may, for example, comprise any suitable corrodible, high reactivity metal. In one embodiment, the first material is magnesium, which is anodic with respect to the intermediate material 26 and second material 20. The first material 18 may includes any material suitable for use in a downhole environment, provided the first material 18 is more galvanically active in the downhole environment relative to the intermediate material 26 and second material 20. In particular, first material 18 may be selected from the materials described herein for use as intermediate material 26, so long as the first material 18 is selected to be more galvanically active than the intermediate material 26.

[0021] The intermediate material 26 may, for example, comprise a corrodible, intermediate reactivity metal. In one embodiment, the intermediate material 26 comprises magnesium, aluminum, manganese or zinc, or an alloy thereof, or a combination comprising at least one of the foregoing. Magnesium alloys include any such alloy which is corrodible in a corrosive environment including those typically encountered downhole, such as an aqueous environment which includes salt (i.e., brine), or an acidic or corrosive agent such as hydrogen sulfide, hydrochloric acid, or other such corrosive agents. Magnesium alloys suitable for use include alloys of magnesium with aluminum (Al), cadmium (Cd), calcium (Ca), cobalt (Co), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), silicon (Si), silver (Ag), strontium (Sr), thorium (Th), zinc (Zn), or zirconium (Zr), or a combination comprising at least one of these elements. Particularly useful alloys can be prepared from magnesium alloy particles including those prepared from magnesium alloyed with Al, Ni, W, Co, Cu, Fe, or other metals. Alloying or trace elements can be included in varying amounts to adjust the corrosion rate of the magnesium. For example, four of these elements (cadmium, calcium, silver, and zinc) have to mild-to-moderate accelerating effects on corrosion rates, whereas four others (copper, cobalt, iron, and nickel) have a still greater accelerating effect on corrosion. Exemplary commercially available magnesium alloys which include different combinations of the above alloying elements to achieve different degrees of corrosion resistance include, but are not limited to, for example, those alloyed with aluminum, strontium, and manganese such as AJ62, AJ50x, AJ51x, and AJ52x alloys, and those alloyed with aluminum, zinc, and manganese which include AZ91A-E alloys.

[0022] It will be appreciated that alloys having corrosion rates greater than those of the above exemplary alloys are contemplated as being useful herein. For example, nickel has been found to be useful in decreasing the corrosion resistance (i.e., increasing the corrosion

rate) of magnesium alloys when included in amounts less than or equal to about 0.5 wt%, specifically less than or equal to about 0.4 wt%, and more specifically less than or equal to about 0.3 wt%, to provide a useful corrosion rate for the corrodible downhole article. The above magnesium alloys are useful for forming the intermediate material 26, and may be formed into the desired shape and size by casting, forging and machining.

[0023] In one embodiment, powders of magnesium or the magnesium alloys described are useful for forming the fixed member 24 as a powder compact. The magnesium alloy powder generally has a particle size of from about 50 to about 250 micrometers (μm), and more specifically about 60 to about 140 μm. The powder may be further coated using a method such as chemical vapor deposition, anodization or the like, or admixed by physical method such as cryo-milling, ball milling, or the like, with a metal or metal oxide, nitride or carbide, such as Al, Ni, W, Co, Cu or Fe, or oxides, nitrides or carbides thereof, or an alloy thereof, or a combination thereof. The coatings may have any suitable thickness, including nanoscale coatings having an average thickness of about 5 nm to about 2500 nm. Such coated powders are referred to herein as controlled electrolytic materials (CEM). The CEM is then molded or compressed into the desired shape by, for example, cold compression or pressing using an isostatic press at about 40 to about 80 ksi (about 275 to about 550 MPa), followed by extrusion, forging, or sintering, or machining, to provide a core having the desired shape and dimensions. The CEM materials may include the cellular nanomatrix materials formed from the powder materials described, for example, in commonly assigned, co-pending US Application Serial Number 12/633,682 filed on December 8, 2009; US Application Serial Number 13/220,824 filed on August 30, 2011; US Application Serial Number 13/220,832 filed on August 30, 2011; and US Application Serial Number 13/220,822 filed on August 30, 2011, which are incorporated herein by reference in their entirety.

[0024] It will be understood that the magnesium alloy or CEM, may thus have any corrosion rate necessary to achieve the desired performance of the article. In a specific embodiment, the magnesium alloy or CEM used to form the fixed member 24 has a corrosion rate of about 0.1 to about 150 mg/cm^2/hour, specifically about 1 to about 15 mg/cm^2/hour using aqueous 3 wt% KCl at 200°F (93°C).

[0025] The second material 20 is, in an embodiment, any material that is galvanically less active (having a lower reactivity than the first material 18 and intermediate material 26), based on, for example, the saltwater galvanic series. The second material 20 may include a

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lower reactivity metal such as various grades of steels, tungsten, chromium, nickel, copper, cobalt, iron, or an alloy thereof, or a combination comprising at least one of the foregoing. In one embodiment, the second material 20 may be substantially non-corrodible or inert in the downhole environment. In another embodiment, the second material 20 may be resistant to corrosion by a corrosive material. As used herein, "resistant" means the second material is not etched or corroded by any corrosive downhole conditions encountered (i.e., brine, hydrogen sulfide, etc., at pressures greater than atmospheric pressure, and at temperatures in excess of 50°C), or any wellbore 70 fluid used in conjunction with the articles or methods described herein.

[0026] By selecting the reactivity of the first and second materials to have a greater or lesser difference in their corrosion potentials, the higher reactivity material (e.g., high reactivity metal) corrodes at a faster or slower rate, respectively. Generally, for metals in the galvanic series, the order of metals, from more noble (i.e., less active and more cathodic) to less noble (i.e., more active and more anodic) includes for example steel, tungsten, chromium, nickel, cobalt, copper, iron, aluminum, zinc, and magnesium.

[0027] When the dissimilar metal combinations described herein are brought into electrical contact in the presence of an electrolyte, an electrochemical potential is generated between the anodic, more galvanically active material and the cathodic, less galvanically active material. The greater the difference in corrosion potential between the dissimilar metals, the greater the electrical potential generated. In such an arrangement, the cathodic material is protected from corrosion by the anodic material, where the anodic material corrodes as a sacrificial anode. Corrosion of the fixed member 24, for example, in brines and other electrolytes can be controlled (eliminated or substantially reduced) when it is in the first position where it is in electrical contact with the more active first section 14. Electrically coupling the anodic material and the cathodic material with an electrolyte also produces an electrical potential that may also be used to power a downhole device, such as, for example, a device for downhole signaling or sensing.

[0028] Referring to FIG. 3, the selectively corrodible article 10 may be used as disclosed herein, and more particularly may be used in accordance with a method 100 of removing a selectively corrodible downhole article 10. The method 100 includes disposing 110 downhole a selectively corrodible downhole article 10, as described herein. The method 100 also includes exposing 120 the selectively corrodible downhole article to a first wellbore fluid 72 while the movable cylindrical member is in the first position, wherein the first section is selectively dissolved. The method 100 further includes moving 130 the movable

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cylindrical member to the second position. The method 100 then includes exposing 140 the selectively corrodible metallic downhole article to a second wellbore 74 fluid, wherein the fixed member is selectively dissolved.

[0029] Disposing 110 the selectively corrodible downhole article 10 downhole may be accomplished in any suitable manner, including delivery downhole by use of a wireline, slickline, tubular string or the like. The movable cylindrical member 12 and fixed member 24 may be disposed downhole as individual components, or together as part of an assembly. Whether as part of the installation or afterwards, the movable cylindrical member 12 is placed in the first position 28 where the first section 14 is disposed on and in electrical contact with the fixed member 24.

[0030] Once the first section 14 is disposed on and in electrical contact with the fixed member 24, the method 100 also includes exposing 120 the selectively corrodible downhole article to a first wellbore fluid 72 while the movable cylindrical member is in the first position, wherein the first section is selectively dissolved. The first wellbore fluid 72 may include an aqueous or non-aqueous electrolyte, depending on the application and controllability of ambient conditions. In the downhole environment, controlling the ambient conditions to exclude moisture is not practical, and hence, under such conditions, the electrolyte is generally an aqueous electrolyte. Aqueous electrolytes may include water or a salt dissolved in water, such as a brine, or an acid, or a combination comprising at least one of the foregoing. Exposing 120 the selectively corrodible downhole article 10 to a first wellbore fluid 72 may include performing a downhole operation, such as a fracking, for example. During exposing 120, the movable cylindrical member 12 is in the first position 28 where the first section 14 is disposed on and in electrical contact with the fixed member 24. In the first position 28, the more galvanically active first material 18 of the first section 14 acts as an anode and is selectively dissolved or corroded while the less galvanically active intermediate material 26 of the fixed member 24 acts as a cathode and is selectively protected from dissolution or corrosion. The movable cylindrical member 12, particularly the first section 14, and the fixed member 24 may be designed for the wellbore operation for which they are to be used to provide sufficient material for the dissolution or corrosion that occurs during the downhole operation that is to be performed.

[0031] The method 100 further includes moving 130 the movable cylindrical member 12 to the second position 30. In the second position 30, the second section 16 is disposed on and in electrical contact with the fixed member 24. In the second position 30, the fixed member 24 is configured for selective dissolution because the intermediate material 26 is

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more galvanically active than the second material 20. In the second position 30, the more galvanically active intermediate material 26 of the fixed member 24 acts as an anode and is selectively dissolved or corroded while the less galvanically active second material 20 of the second section 16 acts as a cathode and is selectively protected from dissolution or corrosion. The fixed member 24 and intermediate material 26 may also be selected and designed for the wellbore operation for which they are to be used, such as to provide rapid dissolution or corrosion and removal from the wellbore 70. Removing the fixed member 24 may, for example, be used to open the wellbore for a subsequent wellbore operation, such as a completion or production operation.

[0032] The method 100 then includes exposing 140 the selectively corrodible metallic downhole article 10 to a second wellbore 74 fluid, wherein the fixed member 24 is selectively dissolved. This may also include the selective dissolution of other members, such as the ball 50 or plug 60, as described herein. The second wellbore fluid may be the same wellbore fluid as the first wellbore fluid 72. Alternately, the second wellbore fluid 74 and first wellbore fluid 72 may be different wellbore fluids.

[0033] All ranges disclosed herein are inclusive of the endpoints, and the endpoints are independently combinable with each other. The suffix "(s)" as used herein is intended to include both the singular and the plural of the term that it modifies, thereby including at least one of that term (e.g., the colorant(s) includes at least one colorants). "Optional" or "optionally" means that the subsequently described event or circumstance can or cannot occur, and that the description includes instances where the event occurs and instances where it does not. As used herein, "combination" is inclusive of blends, mixtures, alloys, reaction products, and the like. All references are incorporated herein by reference.

[0034] The use of the terms "a" and "an" and "the" and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Further, it should further be noted that the terms "first," "second," and the like herein do not denote any order, quantity, or importance, but rather are used to distinguish one element from another. The modifier "about" used in connection with a quantity is inclusive of the stated value and has the meaning dictated by the context (e.g., it includes the degree of error associated with measurement of the particular quantity).

[0035] While one or more embodiments have been shown and described, modifications and substitutions may be made thereto without departing from the spirit and

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scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

CLAIMS

    1.   A selectively corrodible downhole article, comprising:

a movable cylindrical member comprising a first section and an axially separated second section, the first section comprising a first material having a first galvanic activity, the second section comprising a second material having a second galvanic activity, the first galvanic activity being greater than the second galvanic activity, the first section being electrically isolated from the second section; and

a fixed member disposed on the cylindrical member and configured for electrical contact with the first section or the second section, the fixed member comprising an intermediate material having an intermediate galvanic activity, the intermediate galvanic activity being intermediate the first galvanic activity and the second galvanic activity, the movable cylindrical member configured for movement from a first position where the first section is disposed on and in electrical contact with the fixed member and a second position where the second section is disposed on and in electrical contact with the fixed member, wherein in the first position, the first section is configured for selective dissolution, and wherein in the second position, the fixed member is configured for selective dissolution.

    2.   The article of claim 1, wherein the movable member comprises a movable tubular article.

    3.   The article of claim 1, wherein the movable member comprises a slidable sleeve disposed within a tubular article.

    4.   The article of claim 1, wherein the first material comprises magnesium.

    5.   The article of claim 1, wherein the second material comprises steel, tungsten, chromium, nickel, copper, cobalt, iron, or an alloy thereof, or a combination comprising at least one of the foregoing.

    6.   The article of claim 1, wherein the intermediate material comprises magnesium, aluminum, manganese or zinc, or an alloy thereof, or a combination comprising at least one of the foregoing.

    7.   The article of claim 1, wherein the first section comprises a controlled electrolytic material.

    8.   The article of claim 1, wherein the fixed member comprises a controlled electrolytic material.

    9.   The article of claim 1, wherein the fixed member comprises a ball or ball seat.

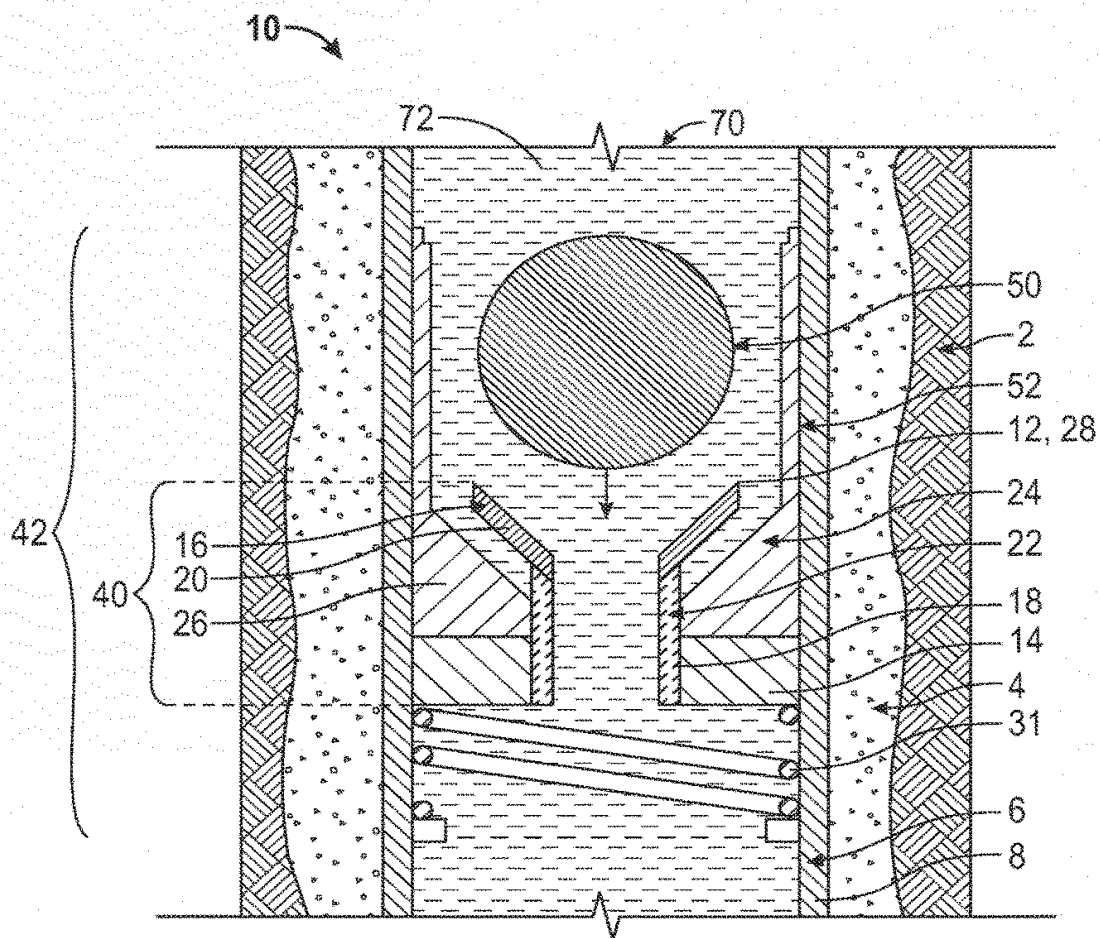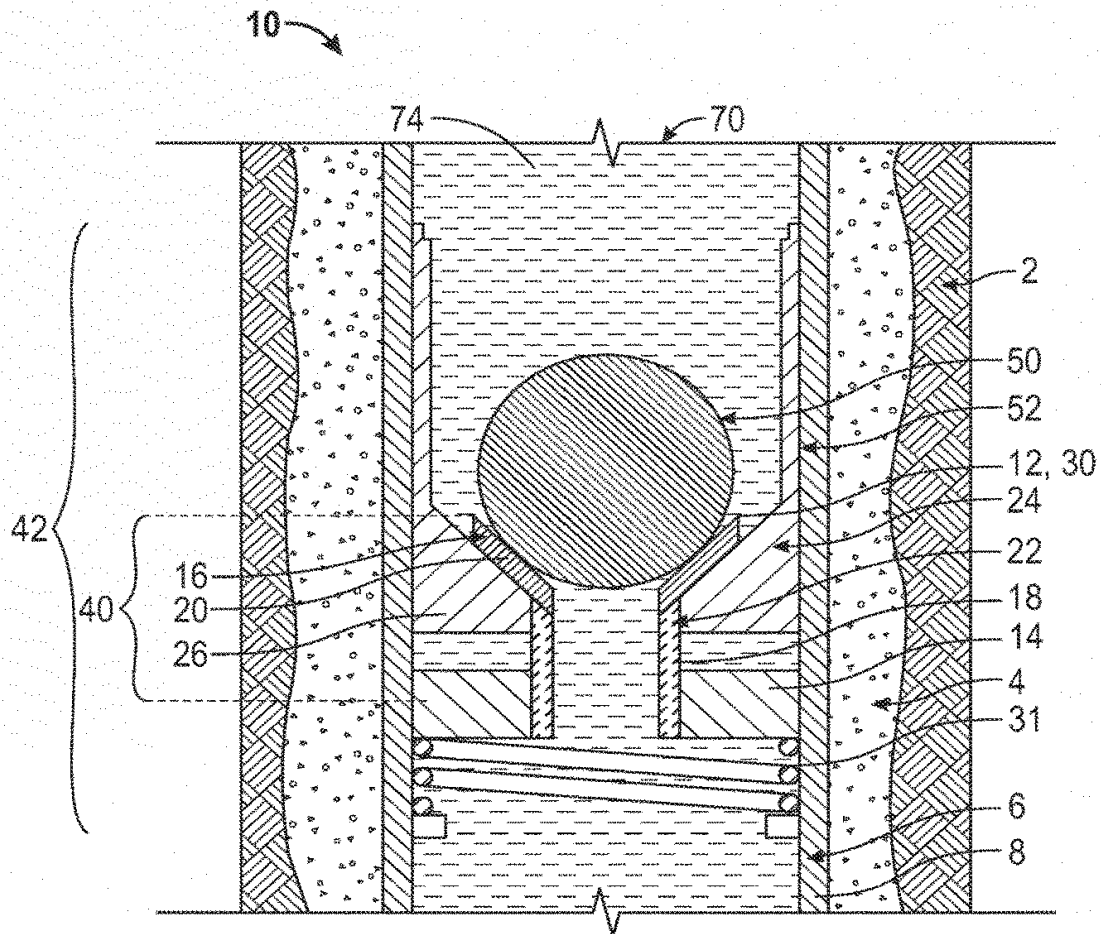   10. The article of claim 1, wherein the fixed member comprises a plug or plug seat.

    11. A method of removing a selectively corrodible downhole article, comprising:

disposing downhole a selectively corrodible downhole article, comprising: a movable cylindrical member comprising a first section and an axially separated second section, the first section comprising a first material having a first galvanic activity, the second section comprising a second material having a second galvanic activity, the first galvanic activity being greater than the second galvanic activity, the first section being electrically isolated from the second section; and a fixed member disposed on the cylindrical member and configured for electrical contact with the first section or the second section, the fixed member comprising an intermediate material having an intermediate galvanic activity, the intermediate galvanic activity being intermediate the first galvanic activity and the second galvanic activity, the movable cylindrical member configured for movement from a first position where the first section is disposed on and in electrical contact with the fixed member and a second position where the second section is disposed on and in electrical contact with the fixed member, wherein in the first position, the first section is configured for selective dissolution, and wherein in the second position, the fixed member is configured for selective dissolution;

exposing the selectively corrodible downhole article to a first wellbore fluid while the movable cylindrical member is in the first position, wherein the first section is selectively dissolved;

moving the movable cylindrical member to the second position; and

exposing the selectively corrodible metallic downhole article to a second wellbore fluid, wherein the fixed member is selectively dissolved.

12. The method of claim 11, wherein the fixed member is selectively dissolved sufficiently to remove it from the selectively corrodible downhole article.

13. The method of claim 11, wherein the first wellbore fluid and the second wellbore fluid are the same fluid.

14. The method of claim 11, wherein the first wellbore fluid and the second wellbore fluid are different fluids.

15. The article of claim 1, wherein the movable member comprises a movable tubular article.

16. The article of claim 1, wherein the movable member comprises a slidable sleeve dispose on or within a tubular article.

17. The article of claim 1, wherein the first material comprises magnesium.

14

18. The article of claim 1, wherein the second material comprises steel, tungsten, chromium, nickel, copper, cobalt, iron, or an alloy thereof, or a combination comprising at least one of the foregoing.

19. The article of claim 1, wherein the intermediate material comprises magnesium, aluminum, manganese or zinc, or an alloy thereof, or a combination comprising at least one of the foregoing.

20. The article of claim 1, wherein the first section comprises a controlled electrolytic material.

21. The article of claim 1, wherein the fixed member comprises a controlled electrolytic material.

22. The article of claim 1, wherein the fixed member comprises a ball or ball seat.

23. The article of claim 1, wherein the fixed member comprises a plug or plug seat.
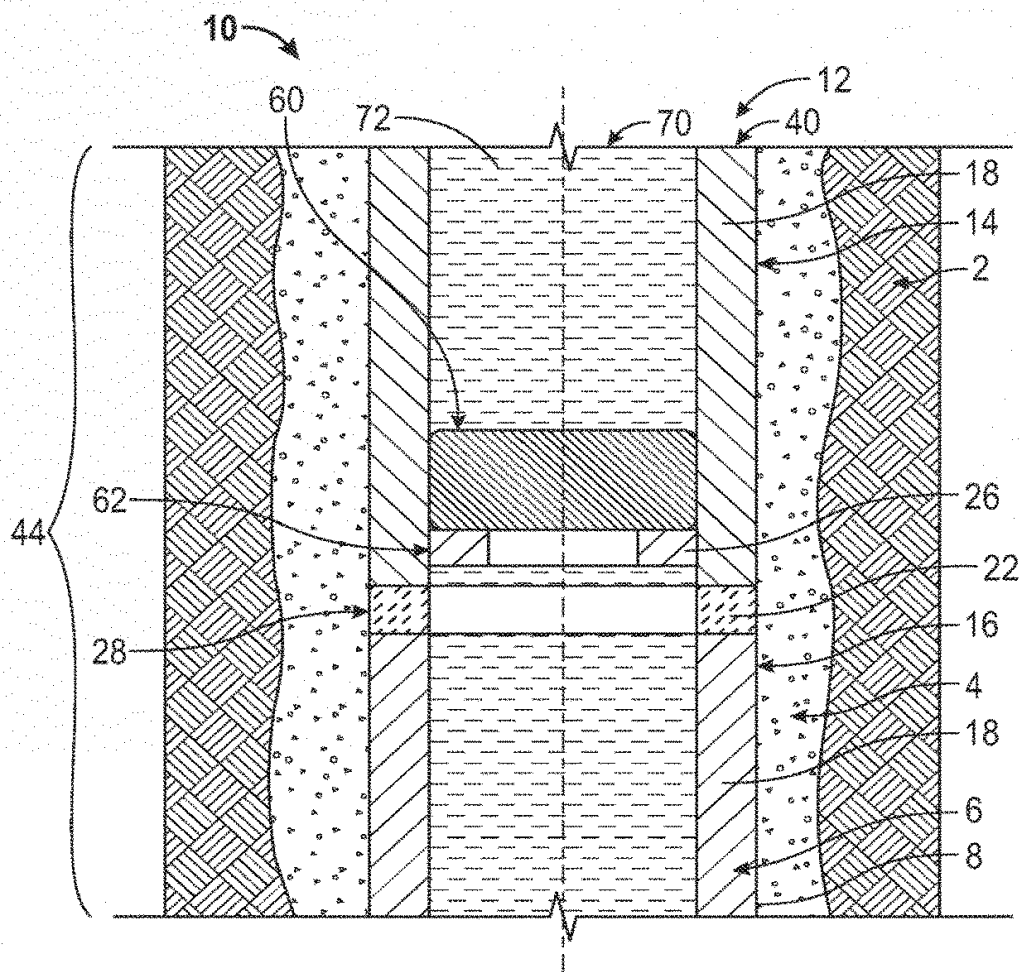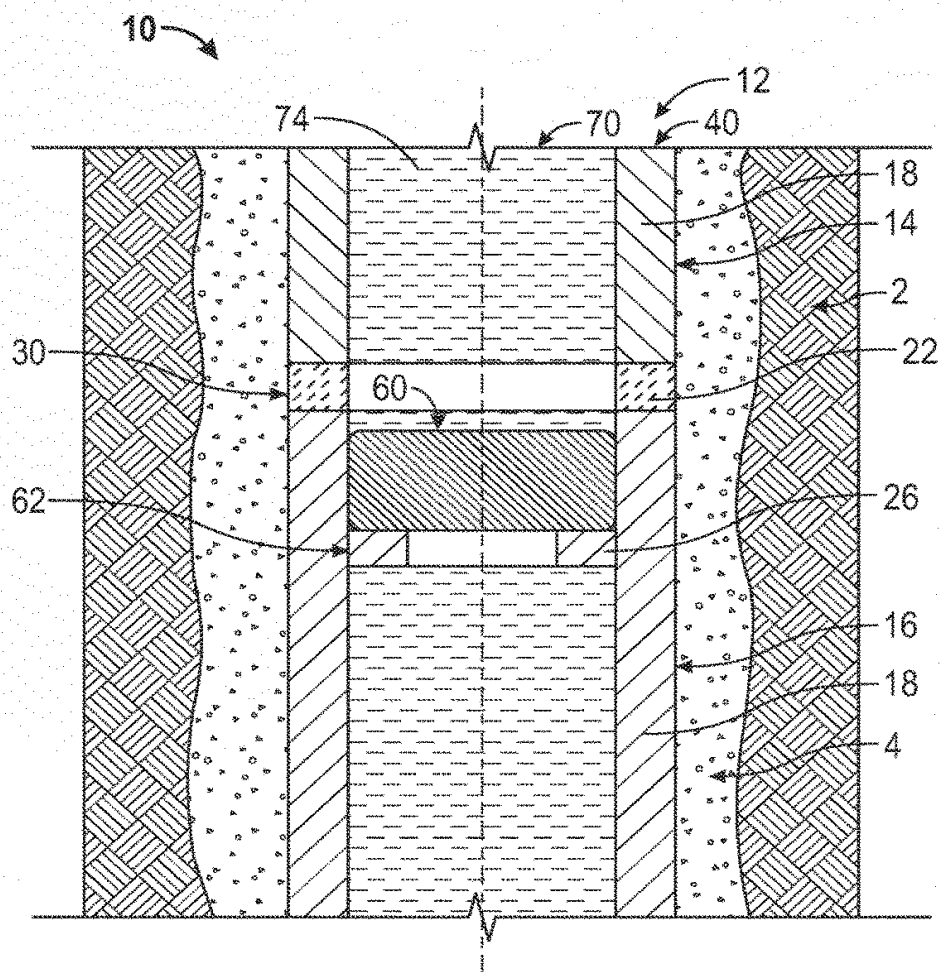
FIG. 1A

FIG. 1B

FIG. 2A

FIG. 2B

100

110

Disposing Selectively Corrodible Article Downhole

120

Exposing Downhole Article to First Wellbore Fluid

130

Moving the Movable Cylindrical Member to the
Second Position

140

Exposing Downhole Article to Second
Wellbore Fluid
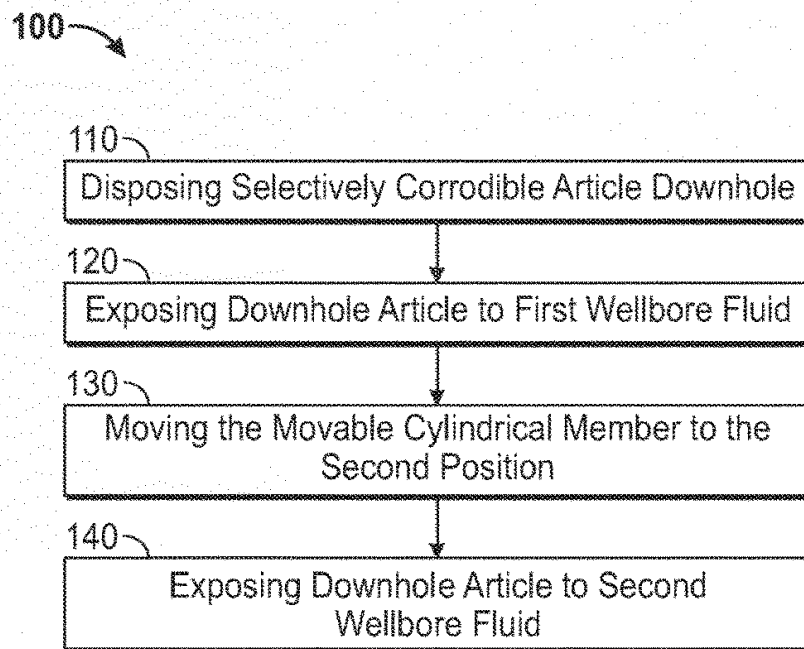
FIG. 3

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

E21B 34/08(2006.01)i, E21B 43/12(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: E21B 34/08; E21B 34/06; E21B 36/04; C22C 24/00; E21B 41/00; E21B 33/13; E21B 29/00; C22C 21/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: corrodible downhole article, movable cylindrical member, fixed member, galvanic activity, and wellbore fluid

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2008-0066924 A1 (YANG XU) 20 March 2008 See paragraphs [0027]-[0028], [0035] and figures 1-4.	1-23
A	US 2007-0181224 A1 (MANUEL P. MARYA et al.) 09 August 2007 See paragraphs [0056]-[0057] and figures 2A-2B.	1-23
A	US 2010-0294510 A1 (KEVIN C. HOLMES) 25 November 2010 See paragraphs [0021]-[0022] and figure 5.	1-23
A	US 5607017 A (STEVE OWENS et al.) 04 March 1997 See column 2, line 37 - column 3, line 27 and figure 2.	1-23
A	US 5479986 A (JOHN C. GANO et al.) 02 January 1996 See column 6, lines 24-45 and figure 1B.	1-23

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

*	Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	
"E"	earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	
"P"	document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 April 2013 (29.04.2013)	**29 April 2013 (29.04.2013)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon Metropolitan City, 302-701, Republic of Korea Facsimile No. 82-42-472-7140	CHOI, Sang Won Telephone No. 82-42-481-8291

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Form PCT/ISA/210 (patent family annex) (July 2009)

(54) Title: METHOD OF MAKING A METALLIC POWDER AND POWDER COMPACT AND POWDER AND POWDER
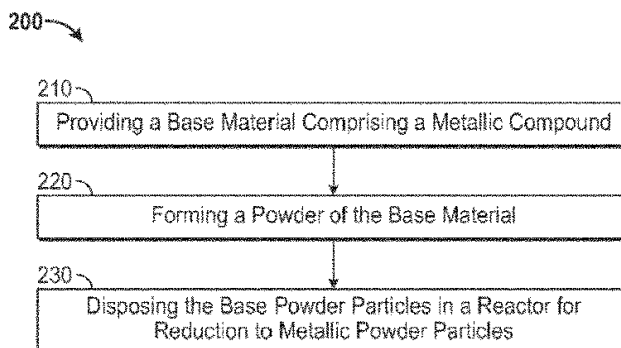COMPACT MADE THEREBY

FIG. 1

(57) Abstract: A method of making a nanoscale metallic powder is disclosed. The method includes providing a base material com-
prising a metallic compound, wherein the base material is configured for chemical reduction by a reductant to form a metallic materi-
al. The method also includes forming a powder of the base material, the powder comprising a plurality of powder particles, the
powder particles having an average particle size that is less than about 1 micron. The method further includes disposing the powder
particles into a reactor together with the reductant under an environmental condition that promotes the chemical reduction of the
base material and formation of a plurality of particles of the metallic material.

METHOD OF MAKING A METALLIC POWDER AND POWDER COMPACT AND POWDER AND POWDER COMPACT MADE THEREBY

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Application No. 13/397492, filed on February 15, 2012, which is incorporated herein by reference in its entirety.

BACKGROUND

[0002] Well drilling, completion and production operations, such as those employed for oil and natural gas wells and carbon sequestration, often utilize wellbore components or tools that, due to their function, are only required to have limited service lives that are considerably less than the service life of the well. After a component or tool service function is complete, it must be removed or disposed of in order to recover the original size of the fluid pathway for use, including hydrocarbon production, CO_2 sequestration, etc. Disposal of components or tools has conventionally been done by milling or drilling the component or tool out of the wellbore, which are generally time consuming and expensive operations, particularly in horizontal sections of the wellbore.

[0003] In order to eliminate the need for milling or drilling operations, the removal of components or tools by dissolution or corrosion using controlled electrolytic materials, such as those having a cellular nanomatrix that can be selectively and controllably degraded or corroded in response to a wellbore environmental condition, such as exposure to a predetermined wellbore fluid, as been described in, for example, U.S. Patent Application Serial No. 12/633,688 filed December 8, 2009, entitled METHOD OF MAKING A NANOMATRIX POWDER METAL COMPACT.

[0004] The use of controlled electrolytic materials formed as powder compacts from metal powders to manufacture various downhole tools and components makes it very desirable to develop improved metal powders used to form the compacts and improved, cost effective methods of making the metal powders in high volumes, as well as improved methods of using them to form powder metal compacts.

SUMMARY

[0005] In an exemplary embodiment, a method of making a nanoscale metallic powder is disclosed. The method includes providing a base material comprising a metallic compound, wherein the base material is configured for chemical reduction by a reductant to form a metallic material. The method also includes forming a powder of the base material, the powder comprising a plurality of powder particles, the powder particles having an average particle size that is less than about 1 micron. The method further includes disposing

the powder particles into a reactor together with the reductant under an environmental condition that promotes the chemical reduction of the base material and formation of a plurality of particles of the metallic material.

[0006] In another exemplary embodiment, a metallic powder is disclosed. The metallic powder comprises a plurality of powder particles comprising magnesium or aluminum, or a combination thereof, wherein the powder particles have a predetermined particle morphology resulting from reduction from a magnesium compound or an aluminum compound, or a combination thereof, respectively.

[0007] In yet another exemplary embodiment, a method of making a powder metal compact is disclosed. The method includes providing a metallic powder that comprises a plurality of powder particles comprising magnesium or aluminum, or a combination thereof, by direct reduction of a base powder comprising a plurality of powder particles of a magnesium compound or an aluminum compound, or a combination thereof, respectively, the base powder particles having an average particle size that is less than about 1 micron. The method also includes depositing a nanoscale metallic coating layer of a metallic coating material on outer surfaces of the metallic powder particles to form coated metallic powder particles. The method further includes forming a powder metal compact by sintering of the nanoscale metallic coating layers of the plurality of coated metallic powder particles to form a substantially-continuous, cellular nanomatrix of the metallic coating material and a plurality of dispersed particles comprising the metallic powder particles dispersed within the cellular nanomatrix.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Referring now to the drawings wherein like elements are numbered alike in the several Figures:

[0009] FIG. 1 is a flowchart of an exemplary embodiment of a method of making a metallic powder as disclosed herein;

[0010] FIG. 2 is a flowchart of an exemplary embodiment of a method of making a powder compact from a metallic powder as disclosed herein;

[0011] FIG. 3 is a schematic cross-sectional view illustrating an exemplary embodiment of a method of making metallic powders as disclosed herein, as well as the compound powder particles used and metallic particles formed according to the method;

[0012] FIG. 4 is a schematic cross-sectional view illustrating a second exemplary embodiment of a method of making a metallic powders as disclosed herein;

[0013] FIG. 5 is a schematic cross-sectional view illustrating a third exemplary embodiment of a method of making a metallic powder as disclosed herein;

[0014] FIG. 6 is a schematic cross-sectional view of coated metallic powder particles as disclosed herein; and

[0015] FIG. 7 is a schematic cross-sectional view of a powder compact as disclosed herein.

DETAILED DESCRIPTION

[0016] Referring to the Figures, more particularly FIGS. 1-7, a method 200 for making metallic powders 10, such as magnesium and aluminum metallic powders 10, suitable for use to form controlled electrolytic material (CEM) powder compacts 100 and a method of making 300 the electrolytic material (CEM) powder compacts 100 are disclosed. The metallic powders 10, such as magnesium and aluminum metallic powders 10, are formed directly from metallic compound powders 30, such as magnesium compound and aluminum compound powders 30, by the chemical reduction of these powders. These metallic powders 10 are structured in that they have powder particle morphologies or structures that are defined by the precursor compound powders 30, such as magnesium compound and aluminum compound powders, and the reducing agent or reductant selected and the method 200 used to make them. These structured metallic powders may have what may be termed as molecular powder particle morphologies or structures that include very fine particle sizes down to about 1 nm, particle clusters of these fine particles, porous particles and other shapes and features that are defined by the chemical reduction of the metallic portion of the compound powders 30 and the removal of the non-metallic portion of the compound powders 30 as reactant species. Powder compacts 100 formed from these metallic powders 10 may have a fine grain structure and display high ultimate compressive strength, because the movement of dislocations in such materials is hindered by the grain boundaries, which may be defined in part by the fine particle size of the metallic powders 10 used to form the compacts. High ultimate compressive strength may also be aided by the formation of intermetallic phases that may result during the formation of the compacts, as well as nanostructuring imparted to the metallic powder particles after they are formed as described herein.

[0017] Referring FIGS. 1 and 3-7, a method 200 of making nanoscale metallic powder 10, including nanoscale magnesium or aluminum metallic powder 10, is disclosed. The method 200 includes providing 210 a base material comprising a metallic compound, such as a magnesium compound or an aluminum compound, or a combination thereof,

wherein the base material is configured for chemical reduction by a reductant 20 to form a metallic material 12 comprising powder particles 14. The method also includes forming 220 a powder 30 of the base material 32, the powder 30 comprising a plurality of powder particles 34, the powder particles 34 having an average particle size that is less than about 1 micron. The method 200 also includes disposing 230 the powder particles 34 in a reactor 22 together with the reductant 20 under an environmental condition 24 that promotes the chemical reduction of the base material and formation of a plurality of metallic powder particles 14 of the metallic material 12.

[0018] Providing 210 the base material comprising the metallic compound, such as a magnesium compound or an aluminum compound, or a combination thereof, wherein the base material is configured for chemical reduction by a reductant 20 to form a metallic material 12 may be accomplished by selecting a suitable metallic compound, such as a compound of magnesium or aluminum, or a combination of magnesium and aluminum compounds. Any suitable metallic compound, including various magnesium or aluminum compounds, may be selected that is capable of being reduced by suitable reductant 20 to form a metallic material such as, for example, magnesium or aluminum.

[0019] The base material 32 and metallic compound selected may include any suitable metallic compound. This includes compounds of various alkali metals, alkaline earth metals, transition metals, post transition metals and metalloids. Of these, compounds of magnesium and aluminum are particularly desirable for use to to form metallic powders that can be used to provide CEM materials, as described herein.

[0020] As one example, the base material 32 and the metallic compound may include a magnesium compound and the plurality of metallic powder particles 14 of the metallic material 12 formed upon reduction of the base material 32 to form metallic powder 10 may include magnesium, or more particularly a magnesium alloy, or a combination thereof. The metallic material 12 may also include magnesium oxides, carbides or nitrides, or combinations thereof, as well as various intermetallic compounds comprising magnesium that may also be formed during the chemical reduction of the magnesium compound. Suitable magnesium compounds include magnesium chloride, magnesium fluoride, magnesium iodide, magnesium bromide, magnesium nitride, magnesium nitrate, magnesium bicarbonate, magnesium oxide, magnesium peroxide, magnesium selenide, magnesium telluride or magnesium sulfide, or a combination thereof. Suitable magnesium compounds may also include those which include other metallic elements in addition to magnesium.

[0021] As another example, the base material 32 selected may include an aluminum compound and the plurality of metallic powder particles 14 of the metallic material 12 formed upon reduction of the base material 32 to form metallic powder 10 may include aluminum, or more particularly an aluminum alloy, or a combination thereof. The metallic material 12 may also include aluminum oxides, carbides or nitrides, or combinations thereof, as well as various intermetallic compounds comprising aluminum that may also be formed during the chemical reduction of the aluminum compound. Suitable aluminum compounds include aluminum borate, aluminum bromide, aluminum chloride, aluminum iodide, aluminum fluoride, aluminum hydroxide, aluminum nitride, aluminum nitrate, aluminum oxide, aluminum phosphate, aluminum selenide, aluminum sulfate, aluminum sulfide, aluminum telluride or a combination thereof. Suitable aluminum compounds may also include those which include other metallic elements in addition to aluminum.

[0022] As yet another example, the base material 32 selected may include an aluminum compound and a magnesium compound in the plurality of metallic powder 10 particles of the metallic material 12 formed upon reduction of the base material 32 may include aluminum and magnesium as discrete particles, or as particles that include an alloy, intermetallic compound, or other combination of aluminum and magnesium. The selection of a base material 32 that includes a magnesium compound and an aluminum compound may also, upon reduction, provide a plurality of particles of the metallic material 12 that include magnesium or a magnesium alloy and aluminum or an aluminum alloy, or a combination thereof. Reduction of both aluminum and magnesium together will require selection of a suitable reductant 20 and environmental conditions 24 that enable reduction of both the aluminum compound and a magnesium compound, which in one embodiment may include reduction of both the aluminum compound and the magnesium compound at the same time.

[0023] Forming 220 a powder 30 of the base material 32 may be accomplished by any suitable method for forming a powder of the base material 32 using any suitable powder forming apparatus. Base materials 32 of the types described herein may be provided in various forms, including in the form of particulates of various average sizes that are larger than the sizes desired for use in accordance with method 200. Therefore, forming 220 may be used to reduce the average particle size to a size suitable for use in accordance with the method. In one embodiment, the powder 30 may be formed by ball milling the base material 32 to reduce the average particle size, and more particularly may be formed by cryomilling. The powder 30 of the base material 32 will have a particle size, such as an average particle size, which is selected to produce nanoscale metallic powder 10 particles upon reduction,

which are defined herein as particles having a size less than about 1 micron, including an average particle size less than about 1 micron. In one embodiment, the powder 30 of the base material 32 may include powder particles 34 having a particle size sufficient to produce nanoscale metallic powder particles 14 upon chemical reduction, as described herein, and in another embodiment may have an average particle size that is less than about 1 micron, and in yet another embodiment may have an average particle size that is less than about 0.5 microns.

[0024] The method 200 also includes disposing 230 the powder particles 34 of the base powder 30 in a reactor 22 together with the reductant 20 under an environmental condition 24 that promotes the chemical reduction of the base material 32 and formation of a plurality of metallic powder particles 14 of the metallic material 12. The powder particles 34 may be reduced using any suitable combination of reductant, reactor 22 and environmental condition or conditions 24. Several exemplary embodiments are described below.

[0025] Any suitable reductant 20 may be utilized that is capable of reducing the metallic compound, such as an aluminum compound or a magnesium compound, or a combination thereof, selected to produce the desired metallic material 12. In one embodiment, the reductant 20 may include elements listed in Group I of the periodic table of the elements. Of the Group I elements, hydrogen and potassium are particularly desirable due to their high reactivity and relative abundance. The use of hydrogen as a reductant may include hydrogen or a hydrogen compound, and more particularly may include hydrogen gas. Suitable hydrogen compounds may include various hydrocarbons, hydrides such as lithium triethylborohydride, lithium borohydride, sodium borohydride, lithium aluminium hydride, diisobutylaluminium hydride, as well as various hydrogen-nitrogen compounds, such as ammonia, various ammonium compounds, hydrazine and others, that are configured to provide hydrogen anion (hydride ion) or hydrogen in amounts and chemical forms suitable for use as reductant 20. It will be understood that the selection and use of various hydrogen, potassium or other Group I compounds may require various intermediate reactions to liberate hydrogen anion (hydride ion), hydrogen or another Group I element so that it is available for use in the reduction of the base material 32.

[0026] Any suitable environmental condition or combination of conditions 24 may be employed to promote the reduction reaction necessary to reduce base material 32 and provide metallic material 12. In one embodiment, heat will be provided to raise the temperature to promote the reduction reaction. In another embodiment, the atmosphere within the reactor 22 will be controlled to limit the reactant species available within the reactor, such as by

operating the reactor at a predetermined pressure, including a pressure that is lower than ambient atmospheric pressure, to lower the partial pressures of various reactants such as, for example, oxygen or nitrogen, or both of them. For example, it is important to effectively remove the products of the reduction reactions other than the desired product powder (such as H_2O, HCl, HBr, etc.) from the reactor to prevent the reverse reactions from occurring. The atmosphere of the reactor may also be controlled to exclude various reactant species, such as nitrogen or oxygen, or both of them, by the use of an inert carrier gas such as helium, argon or the like, wherein the reductant 20, such as hydrogen may be introduced together with the inert gas, such as by a gas flow through a sealed reactor that removes any undesirable reactant species and provides only a supply of predetermined reactant species, such as the reductant 20, for reaction with the base material 32. In other embodiments, the predetermined environmental conditions may include a predetermined temperature, predetermined pressure, predetermined reactant species, predetermined electric field, predetermined electric current or predetermined voltage, or a combination thereof.

[0027] The plurality of particles of the metallic material 12 formed by the chemical reduction of the compound powder particles 30 of the base material 32 may have any suitable particle size. In one embodiment the compound particles 30 of the base material 32, reductant 20 and environmental conditions 24 may be selected to provide an average particle size of the metallic powder 10 particles that is less than the particle size of the compound powder particles 30 of the base material 32. In another embodiment, the compound particles 30 of the base material 32, reductant 20 and environmental conditions 24 may be selected to provide an average particle size of the metallic powder 10 particles that is greater than the particle size of the compound powder particles 34 of the base material 32, such as where the metallic powder particles 14 produced by the reduction reaction agglomerate or otherwise combine with one another to produce metallic powder particles 14 that have a particle size greater than the compound powder particles 34 of the base material 32 from which they were reduced. In one example, metallic powder particles 14 reduced from different compound powder particles 34 may be fused to one another by metallic bonds, such as where the reduction reaction produces molten metallic powder particles 14 and one or more particles impact one another in the molten state and become metallurgical bonded or fused to one another. In another example, metallic powder particles 14 reduced from different compound powder particles 34 may cluster together due to interparticle attractive forces of various types, including van der Waals forces, electrostatic forces, and metallic and chemical bonds associated with surface adducts that may result from the reduction or other reactions within

the reactor 22, or after the reduction reaction has been completed. While the method 200, and more particularly the compound powder particles 34, reductant 20 and environmental conditions 24 and reduction reaction, may be designed to produce metallic powder particles 14 having various particle sizes, it is particularly desirable that the method 200 be used to produce nanoscale metallic powder particles 14 for use in the manufacture of powder compacts 100 as described herein. In one embodiment, the plurality of metallic powder particles 14 of the metallic material 12 may have an average particle size of about 1 nm to about 1 micron. In another embodiment, the plurality of metallic powder particles 14 of the metallic material 12 may have an average particle size of about 5 nm to about 500 nm. In yet another embodiment, method 200 may be utilized to make very fine metallic powder particles 14 having an average particle size of about 1 nm to about 100 nm, and more particularly about 1 nm to about 50 nm, and even more particularly about 1 nm to about 15 nm.

[0028] Due to their formation by reduction of compound powder particles 34, the metallic powder particles 14 of the metallic material 12 have a particle morphology that is determined by the particle morphology or structure of the compound powder particles 34 (e.g., particle size and shape), and since these particles may be selected to have very small particle sizes as described herein, this may also include the molecular structure of the base material 32. In one embodiment, the metallic powder particles 14 may have a substantially spherical particle morphology, particularly where the reduction reaction may involve melting of the particles wherein surface tension effects may influence the particle morphology. In other embodiments, various types of particle agglomeration may result, as described herein, and produce fused particles or particle clusters. In yet another embodiment, the reduction reaction together with the molecular structure of the base material 32 may provide various porous particle morphologies upon reduction and removal of the non-metallic portion of the compound powder particles 34 of the base material 32 resulting in metallic powder particles 14 that include a porous network of the metallic material 12, wherein these particles may have an overall shape that reflects the shape of the compound powder particles 34, but are comprised of a porous network of the metallic material 12. As an example, the compound powder particles 34 may have a substantially spherical, flat planar, platelet or irregular structure defined by their crystal or molecular structure and the methods used to produce them, such as ball milling or cryomilling.

[0029] Disposing 230 the powder particles 34 of the base powder 30 in a reactor 22 together with the reductant 20 under an environmental condition 24 that promotes the chemical reduction of the base material 32 and formation of a plurality of metallic powder

particles 14 of the metallic material 12 may be performed in any suitable reactor 22 using any combination of base material 32, reductant 20 and environmental conditions 24.

[0030] In one embodiment, the method 200 comprises disposing 230 the compound powder particles 34 in a fluidized bed reactor 50, wherein the powder particles comprise a fluidized bed 52 of powder particles and the reductant 20 comprises a fluid 54 that is configured to flow through and form the fluidized bed 52 of powder particles, as illustrated schematically in FIG. 3. In an exemplary embodiment, the fluid may include hydrogen gas or a hydrogen compound as described herein. The environmental condition 24 may include heating the fluidized bed 52, the fluid 54, or both, to a predetermined temperature sufficient to chemically reduce the powder particles and form the metallic material particles 14. The reaction may be performed as a batch reaction where the bed of compound powder particles 34 is established and the reduction reaction proceeds until the entire bed, or a portion thereof, is converted to metallic powder particles 14. Alternately, the reaction may be performed as a continuous reaction where the bed of compound powder particles 34 is continuously, or at predetermined intervals, replenished as the reduction reaction proceeds and the metallic powder particles 14 are separated in the bed, such as by density differences, are continuously, or at predetermined intervals, removed from the reactor 22. The chemical compounds and species 56 resulting from the reduction reaction may be exhausted from the reactor in any suitable manner.

[0031] In another embodiment, disposing 230 the compound powder particles 34 into a reactor 22, such as a column reactor 60, includes spraying the compound powder particles 34 into the reactor to provide a stream of powder particles 58 and providing a flow, such as a countercurrent flow, of the reductant 20 as a fluid 54 through the reactor 22, as illustrated schematically in FIG. 4. In one embodiment, this may include a stream of molten powder particles 58. The flow of the reductant 20 through the reactor impinges upon the stream 58 of compound powder particles 34 facilitating the reduction of the particles. The environmental condition 24 may include, heating the stream 58 of powder particles and the reductant 20 to a predetermined temperature sufficient to chemically reduce the compound powder particles 34 and form the metallic powder particles 14 of the metallic material 12. In one embodiment, this may be accomplished by heating a portion 62 of the column reactor 60 with a heater 64. In this embodiment, the reductant 20 may include hydrogen or a hydrogen compound, and more particularly may include hydrogen gas, as well as an inert carrier gas. In this embodiment, the method 200 may also include, prior to spraying, combining the compound powder particles 34 with a liquid carrier to form a slurry 59 in order to disperse the particles

in the liquid, wherein spraying the compound powder particles comprises spraying the slurry 59. Some powder 34 may dissolve in the carrier fluid (like Mg salt in water). This jet will evaporate in the reactor and may produce fine particles of Mg salt. The liquid carrier may include any suitable liquid carrier, and may include an organic or an inorganic liquid, or a combination thereof. An example of an inorganic liquid includes various aqueous liquids. As another example, the carrier may include a hydrocarbon liquid and may be selected to provide a source for hydrogen as a reductant 20.

[0032] In a further embodiment, disposing 230 the compound powder particles 34 into a reactor 22 may include placing the compound powder particles 34 into a furnace 70, such as one of a batch furnace (FIG. 5), continuous furnace (not shown) or rotatable kiln (not shown). Disposing 230 may also include providing a flow of the reductant 20 as a fluid 54 through the furnace 70 as reactor 22, wherein the flow of the reductant 20 through the reactor exposing the compound powder particles 34 to the reductant 20. In this embodiment, the environmental condition 24 may also include heating the compound powder particles 34 and the reductant 20 in the furnace to a predetermined temperature sufficient to chemically reduce the compound powder particles 34 and form the metallic powder particles 14. In this embodiment, the reductant 20 may also include hydrogen or a hydrogen compound. The compound particles 34 are, for example, inserted as a batch at a time (t_1) and upon exposure to the reductant for a time sufficient to complete the reduction of the batch, the metallic powder particles 14 may be removed at a time (t_2).

[0033] Once the metallic powder particles 14 have been formed, they may be used in a method 300 of making a powder metal compact 100, as described further below and illustrated in FIG. 7. The method 300 includes providing 310 a metallic powder 10 that comprises a plurality of metallic powder particles 14 that include magnesium particles or aluminum particles, or a combination thereof, as described herein, by direct reduction of a base powder 30 comprising a plurality of compound powder particles 34 of a metallic compound or metallic compounds, such as a magnesium compound or an aluminum compound, or a combination thereof, respectively, wherein the base powder particles 34 have an average particle size that is less than about 1 micron, and more particularly, from about 1 nm to less than about 1000 nm. In another embodiment, this may also include metallic compounds of Fe, Co, Cu, Ni, etc. as cathodic centers. The size of these inclusions can be from nm to micrometer in size. The method 300 also includes depositing 320 a nanoscale metallic coating layer 16 of a metallic coating material 18 on outer surfaces 19 of the metallic powder particles 14 to form coated metallic powder particles 15 as shown in FIG. 6. The

method 300 further includes forming 330 a powder metal compact 100 by compaction of the
nanoscale metallic coating layers 16 of the plurality of coated metallic powder particles 15 to
form a substantially-continuous, cellular nanomatrix of the metallic coating material 17 and a
plurality of dispersed particles comprising the metallic powder particles 14 dispersed within
the cellular nanomatrix as illustrated in FIG. 7.

[0034] Providing 310 a metallic powder 10 that comprises a plurality of metallic
powder particles 14 that include magnesium particles or aluminum particles, or a
combination thereof, as described herein, by direct reduction of a base powder 30 comprising
a plurality of compound powder particles 34 of a magnesium compound or an aluminum
compound, or a combination thereof, respectively, wherein the base powder particles 34 have
an average particle size that is less than about 1 micron has already been described herein in
conjunction with method 200.

[0035] Depositing 320 a nanoscale metallic coating layer 16 of a metallic coating
material 18 on outer surfaces 19 of the metallic powder particles 14 to form coated metallic
powder particles 15 as shown in FIG. 6 may be performed by any suitable deposition method
and apparatus, including various physical vapor deposition (PVD) methods, such as
sputtering, electron beam evaporation, thermal evaporation, pulsed laser deposition and
cathodic arc deposition, and chemical vapor deposition (CVD) methods, such as atmospheric
pressure CVD, low-pressure CVD, ultra high vacuum CVD, direct liquid injection CVD,
plasma-enhanced CVD, microwave-plasma-assisted CVD and metalorganic CVD. The
nanoscale metallic coating layers 16 may include those described in co-pending US Patent
Application Serial No. 12/633,682, filed on December 8, 2009, which is incorporated herein
by reference in its entirety. More particularly, in the case of magnesium and magnesium
alloy metallic powder particles 14, the metallic powder particles 14 may, for example,
comprise pure magnesium and various magnesium alloys, including Mg-Zr, Mg-Zn-Zr, Mg-
Al-Zn-Mn, Mg-Zn-Cu-Mn or Mg-W alloys, or a combination thereof, and the various
nanoscale metallic coating layers 16 may include Ni, Fe, Cu, Co, W, Al, Zn, Mn, Mg or Si, or
an oxide, nitride, carbide, intermetallic compound or cermet comprising at least one of the
foregoing, or a combination thereof, as described in co-pending US Patent Application Serial
No. 13/220,824 filed on August 30, 2011, which is incorporated herein by reference in its
entirety. In the case of aluminum and aluminum alloy metallic powder particles 14, the
metallic powder particles 14 may, for example, comprise pure aluminum and various
aluminum alloys, including Al-Cu-Mg, Al-Mn, Al-Si, Al-Mg, Al-Mg-Si, Al-Zn, Al-Zn-Cu,
Al-Zn-Mg, Al-Zn-Cr, Al-Zn-Zr, or Al-Sn-Li alloys, or a combination thereof, and the various

nanoscale metallic coating layers 16 may include Ni, Fe, Cu, Co, W, Al, Zn, Mn, Mg or Si, or
an oxide, nitride, carbide, intermetallic compound or cermet comprising at least one of the
foregoing, or a combination thereof, as described in co-pending US Patent Application Serial
No. 13/220,822 filed on August 30, 2011, which is incorporated herein by reference in its
entirety. The coating layer 16 may be applied to all of the morphological types of metallic
powder particles 14 that may be produced by method 200, including to discrete fine particles
21, particle clusters 23 and to porous particles 25 of various particle shapes (FIG. 6).

[0036] Forming 330 a powder metal compact 100 by compaction of the nanoscale
metallic coating layers 16 of the plurality of coated metallic powder particles 15 to form a
substantially-continuous, cellular nanomatrix of the metallic coating material 18 and a
plurality of dispersed particles comprising the metallic powder particles 14 dispersed within
the cellular nanomatrix may be performed by any forming method and apparatus, including
cold pressing, including cold isostatic pressing (CIP), hot pressing, including hot isostatic
pressing (HIP), forging or extrusion, or a combination thereof. Forming 330 may also
include heating of the powder and/or compact, either while the powder is being formed or
afterward, or both.

[0037] Powder compact 100 includes a cellular nanomatrix of a nanomatrix material
comprising the material of the coating layers 16 that are joined to one another during forming
330 having a plurality of dispersed metallic powder particles 14 dispersed throughout the
cellular nanomatrix. The dispersed metallic powder particles 14 may be equiaxed in a
substantially continuous cellular nanomatrix, or may be substantially elongated or otherwise
distorted by forming 330. In the case where the dispersed metallic powder particles 14 are
substantially elongated, the dispersed metallic powder particles 14 and the cellular
nanomatrix may be continuous or discontinuous. The substantially-continuous cellular
nanomatrix and nanomatrix material formed of sintered metallic coating layers 16 is formed
by the compaction and sintering of the plurality of metallic coating layers 16 of the plurality
of metallic powder particles 14, such as by CIP, HIP, extrusion or dynamic forging, or a
combination thereof. The chemical composition of nanomatrix material may be different
than that of coating material due to diffusion effects associated with the sintering. Powder
metal compact 100 also includes a plurality of dispersed powder particles 14 that comprise
metallic material 12. Dispersed metallic powder particles 14 correspond to and are formed
from the plurality of metallic powder particles 14 and metallic material 12 of the plurality of
metallic powder particles 14 as the metallic coating layers 16 are sintered together to form the
nanomatrix. The chemical composition of the dispersed metallic material 12 may also

change from the composition prior to forming due to diffusion effects associated with sintering.

[0038] As used herein, the use of the term cellular nanomatrix does not connote the major constituent of the powder compact 100, but rather refers to the minority constituent or constituents, whether by weight or by volume. This is distinguished from many matrix composite materials where the matrix comprises the majority constituent by weight or volume. The use of the term substantially-continuous, cellular nanomatrix is intended to describe the extensive, regular, continuous and interconnected nature of the distribution of the nanomatrix material within the powder compact 100. As used herein, "substantially-continuous" describes the extension of the nanomatrix material throughout the powder compact 100 such that it extends between and envelopes substantially all of the dispersed metallic powder particles 14. Substantially-continuous is used to indicate that complete continuity and regular order of the nanomatrix around each dispersed metallic powder particle 14 is not required. For example, defects in the coating layer 16 over metallic powder particles 14 may cause bridging of the metallic powder particles 14 during sintering of the powder compact 100, thereby causing localized discontinuities to result within the cellular nanomatrix, even though in the other portions of the powder compact the nanomatrix is substantially continuous and exhibits the structure described herein. In contrast, in the case of substantially elongated dispersed metallic powder particles 14, such as those formed by extrusion, "substantially discontinuous" is used to indicate that incomplete continuity and disruption (e.g., cracking or separation) of the nanomatrix around each dispersed metallic powder particle 14, such as may occur in a predetermined extrusion direction, or a direction transverse to this direction. As used herein, "cellular" is used to indicate that the nanomatrix defines a network of generally repeating, interconnected, compartments or cells of the nanomatrix (coating layer 16) material that encompass and also interconnect the dispersed metallic powder particles 14. As used herein, "nanomatrix" is used to describe the size or scale of the matrix, particularly the thickness of the matrix between adjacent dispersed particles 14. The metallic coating layers that are sintered together to form the nanomatrix are themselves nanoscale thickness coating layers. Since the nanomatrix at most locations, other than the intersection of more than two dispersed metallic powder particles 14, generally comprises the interdiffusion and bonding of two coating layers 16 from adjacent powder particles 14 having nanoscale thicknesses, the matrix formed also has a nanoscale thickness (e.g., approximately two times the coating layer thickness as described herein) and is thus described as a nanomatrix. Further, the use of the term dispersed metallic powder particles

14 does not connote the minor constituent of powder compact 100, but rather refers to the majority constituent or constituents, whether by weight or by volume. The use of the term dispersed particle is intended to convey the discontinuous and discrete distribution of metallic material 12 within powder compact 100.

[0039] Powder compact 100 may have any desired shape or size, including that of a cylindrical billet, bar, sheet or other form that may be machined, formed or otherwise used to form useful articles of manufacture, including various wellbore tools and components. Forming 330 may be used to form powder compact 100 and deform the metallic powder particles 14 and coating layers 16 to provide the full theoretical density and desired macroscopic shape and size of powder compact 200 as well as its microstructure, or may be used to provide compacted articles having less than full theoretical density. The morphology (e.g. equiaxed or substantially elongated) of the dispersed metallic powder particles 14 and cellular network of coating layers 16 results from sintering and deformation of the powder particles as they are compacted and interdiffuse and deform to fill the interparticle spaces. In one embodiment, the sintering temperatures and forming 330 pressures may be selected to ensure that the density of powder compact 100 achieves substantially full theoretical density.

[0040] In addition, prior to forming 330, the metallic powder particles 14, either prior to depositing 320 of the coating layers 16 or afterwards, may receive mechanical or other treatment to provide nanostructuring within the metallic powder particles 14, or both the metallic powder particles 14 and the coating layers 16, to provide nanostructured metallic powder particles 14. By using nanostructured metallic powder particles 14 during forming 330, the resulting powdered compacts 100 may also comprise a nanostructured material. In an exemplary embodiment, a nanostructured material is a material having a grain size, or a subgrain or crystallite size, less than about 200 nm, and more particularly a grain size of about 10 nm to about 200 nm, and even more particularly an average grain size less than about 100 nm. The nanostructure may include high angle boundaries, which are usually used to define the grain size, or low angle boundaries that may occur as substructure within a particular grain, which are sometimes used to define a crystallite size, or a combination thereof. The nanostructure may be formed in the metallic powder particles 14 and/or coating layers 16 by any suitable method, including deformation-induced nanostructure such as may be provided by ball milling, and more particularly by cryomilling (e.g., ball milling in ball milling media at a cryogenic temperature or in a cryogenic fluid, such as liquid nitrogen). The metallic powder particles 14 may be formed as a nanostructured material by any suitable method, such as, for example, by milling or cryomilling of prealloyed powder particles of the

magnesium or aluminum alloys described herein. The metallic powder particles 14 and/or coating layers 16 may also be formed as a nanostructured material 215 by methods including inert gas condensation, chemical vapor condensation, pulse electron deposition, plasma synthesis, crystallization of amorphous solids, electrodeposition and severe plastic deformation, for example. The nanostructure also may include a high dislocation density, such as, for example, a dislocation density between about 10^{17} m^{-2} and 10^{18} m^{-2}, which may be two to three orders of magnitude higher than similar alloy materials deformed by traditional methods, such as cold rolling. The fine powders formed using the method 200, as well as the unique particle morphologies, including particle clusters and porous particles, may afford additional nanostructuring by virtue of their small size or unique features, since the clusters will tend to form boundaries associated with the metallic powder particles incorporated into the cluster and the porous particles will provide additional boundaries associated with the pores as they closed during forming. This additional nanostructuring is expected to further enhance the mechanical properties of powder compacts 100 formed from these metallic powders 10, such as the ultimate compressive strength, yield strength and the like.

[0041] While one or more embodiments have been shown and described, modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustrations and not limitation.

CLAIMS:

1.   A method of making a nanoscale metallic powder, comprising:

providing a base material comprising a metallic compound, wherein the base material is configured for chemical reduction by a reductant to form a metallic material;

forming a powder of the base material, the powder comprising a plurality of powder particles, the powder particles having an average particle size that is less than about 1 micron; and

disposing the powder particles in a reactor together with the reductant under an environmental condition that promotes the chemical reduction of the base material and formation of a plurality of particles of the metallic material.

2.   The method of claim 1, wherein the base material comprises a magnesium compound or an aluminum compound, or a combination thereof

3.   The method of claim 1, wherein the base material comprises a magnesium compound and the plurality of particles of the metallic material comprise magnesium or a magnesium alloy, or a combination thereof.

4.   The method of claim 1, wherein the magnesium compound comprises magnesium chloride, magnesium fluoride, magnesium iodide, magnesium nitride, magnesium nitrate, magnesium bicarbonate, magnesium oxide, magnesium peroxide, magnesium selenide, magnesium telluride or magnesium sulfide, or a combination thereof.

5.   The method of claim 1, wherein the base material comprises an aluminum compound and the plurality of particles of the metallic material comprise aluminum or an aluminum alloy, or a combination thereof.

6.   The method of claim 1, wherein the aluminum compound comprises aluminum borate, aluminum bromide, aluminum chloride, aluminum hydroxide, aluminum nitride, aluminum oxide, aluminum phosphate, aluminum selenide, aluminum sulfate, aluminum sulfide, aluminum telluride or a combination thereof.

7.   The method of claim 1, wherein the base material comprises a magnesium compound and an aluminum compound and the plurality of particles of the metallic material comprise magnesium or a magnesium alloy and aluminum or an aluminum alloy, or a combination thereof.

8.   The method of claim 1, wherein the reductant comprises a group I element.

9.   The method of claim 1, wherein the reductant comprises hydrogen or a hydrogen compound.

10.   The method of claim 9, wherein the reductant comprises hydrogen gas.

11.   The method of claim 1, wherein the plurality of particles of the metallic material have an average particle size that is less than the particle size of the powder particles.

12.   The method of claim 1, wherein the plurality of particles of the metallic material have an average particle size of about 1 nm to about 1 micron.

13.   The method of claim 12, wherein the plurality of particles of the metallic material have an average particle size of about 5 nm to about 500 nm.

14.   The method of claim 12, wherein the plurality of particles of the metallic material have an average particle size of about 1 nm to about 15 nm.

15.   The method of claim 1, wherein the plurality of particles of the metallic material have a particle morphology that is determined by a molecular structure of the base material.

16.   The method of clam 1, wherein the plurality of particles of the metallic material have a porous particle morphology.

17.   The method of claim 1, wherein disposing the powder particles in a reactor comprises disposing the powder particles into a fluidized bed reactor, wherein the powder particles comprise a fluidized bed of powder particles and the reductant comprises a fluid that is configured to flow through and form the fluidized bed of powder particles.

18.   The method of claim 17, wherein the environmental condition comprises heating the fluidized bed to a predetermined temperature sufficient to chemically reduce the powder particles and form the particles of the metallic material.

19.   The method of claim 18, wherein the reductant comprises hydrogen or a hydrogen compound.

20.   The method of claim 1, wherein disposing the powder particles into a reactor comprises:

        spraying the powder particles into the reactor to provide a stream of powder particles; and

        providing a flow of the reductant through the reactor, the flow of the reductant through the reactor impinging upon the stream of powder particles.

21.   The method of claim 20, wherein the environmental condition comprises heating the stream of powder particles and the reductant to a predetermined temperature sufficient to chemically reduce the powder particles and form the particles of the metallic material.

18

22.   The method of claim 21, wherein the reductant comprises hydrogen or a hydrogen compound.

23.   The method of claim 20, further comprising, prior to spraying, combining the powder particles with a liquid carrier to form a slurry, wherein spraying the powder particles comprises spraying the slurry.

24.   The method of claim 23, wherein the liquid carrier comprises an organic or an inorganic liquid, or a combination thereof.

25.   The method of claim 24, wherein the inorganic liquid comprises an aqueous liquid.

26.   The method of claim 1, wherein disposing the powder particles into a reactor comprises:

disposing the powder particles into the reactor comprises placing the powder particles into a batch furnace, continuous furnace or kiln; and

providing a flow of the reductant through the reactor, the flow of the reductant through the reactor exposing the powder particles to the reductant.

27.   The method of claim 26, wherein the environmental condition comprises heating the stream of powder particles and the reductant to a predetermined temperature sufficient to chemically reduce the powder particles and form the particles of the metallic material.

28.   The method of claim 27, wherein the reductant comprises hydrogen or a hydrogen compound.

29.   The method of claim 1, wherein the environmental condition comprises a predetermined temperature, predetermined pressure, predetermined electric field, predetermined electric current or predetermined voltage, or a combination thereof.

30.   The method of claim 1,   wherein forming a powder of the base material comprises ball milling or cryomilling the base material to form the powder particles.

31.   The method of claim 1,   further comprising ball milling or cryomilling the plurality of particles of the metallic material.

32.   A metallic powder comprises a plurality of powder particles comprising magnesium or aluminum, or a combination thereof, wherein the powder particles have a predetermined particle morphology resulting from reduction from a magnesium compound or an aluminum compound, or a combination thereof, respectively.

33.   The metallic powder of claim 32, wherein the predetermined particle morphology comprises porosity.

34.   The metallic powder of claim 32, wherein the predetermined particle morphology comprises a particle size of about 1 to about 100 nm.

35.   The metallic powder of claim 32, wherein the predetermined particle morphology comprises a particle cluster.

36.   The metallic powder of claim 32, wherein the powder particles comprise nanostructured powder particles.

37.   The metallic powder of claim 32, wherein the powder particles comprise a magnesium core and at least one metallic coating layer comprising Ni, Fe, Cu, Co, W, Al, Zn, Mn, Mg or Si, or an oxide, nitride, carbide, intermetallic compound or cermet comprising at least one of the foregoing, or a combination thereof.

38.   The metallic powder of claim 32, wherein the powder particles comprise an aluminum core and at least one metallic coating layer comprising Ni, Fe, Cu, Co, W, Al, Zn, Mn, Mg or Si, or an oxide, nitride, carbide, intermetallic compound or cermet comprising at least one of the foregoing, or a combination thereof.

39.   A method of making a powder metal compact, comprising:

providing a metallic powder that comprises a plurality of powder particles comprising magnesium or aluminum, or a combination thereof, by direct reduction of a base powder comprising a plurality of powder particles of a magnesium compound or an aluminum compound, or a combination thereof, respectively, the base powder particles having an average particle size that is less than about 1 micron;

depositing a nanoscale metallic coating layer of a metallic coating material on outer surfaces of the metallic powder particles to form coated metallic powder particles; and

forming a powder metal compact by sintering of the nanoscale metallic coating layers of the plurality of coated metallic powder particles to form a substantially-continuous, cellular nanomatrix of the metallic coating material and a plurality of dispersed particles comprising the metallic powder particles dispersed within the cellular nanomatrix.

40.   The method of claim 39, wherein the plurality of particles of the metallic material have an average particle size of about 1 nm to about 1 micron.

41.   The method of claim 40, wherein the plurality of particles of the metallic material have an average particle size of about 5 nm to about 500 nm.

42.   The method of claim 39, wherein the plurality of metallic powder particles have a particle morphology that is determined by a molecular structure of the base powder.

43.   The method of clam 39, wherein the plurality of metallic powder particles have a porous particle morphology.

44.   The method of claim 39, further comprising ball milling or cryomilling the plurality of metallic powder particles, wherein the metallic powder particles comprise nanostructured powder particles.

45.   The method of claim 39, wherein forming comprises cold pressing, hot pressing, forging or extrusion, or a combination thereof.
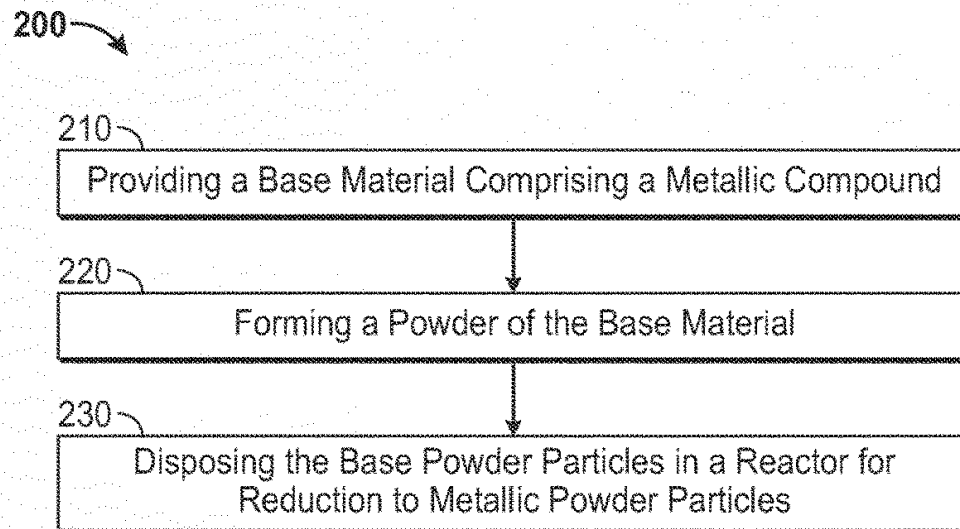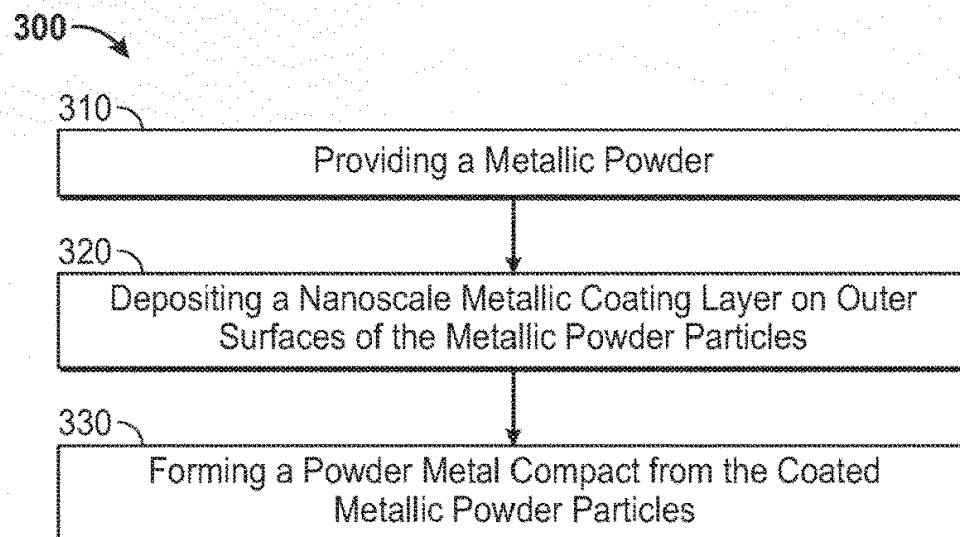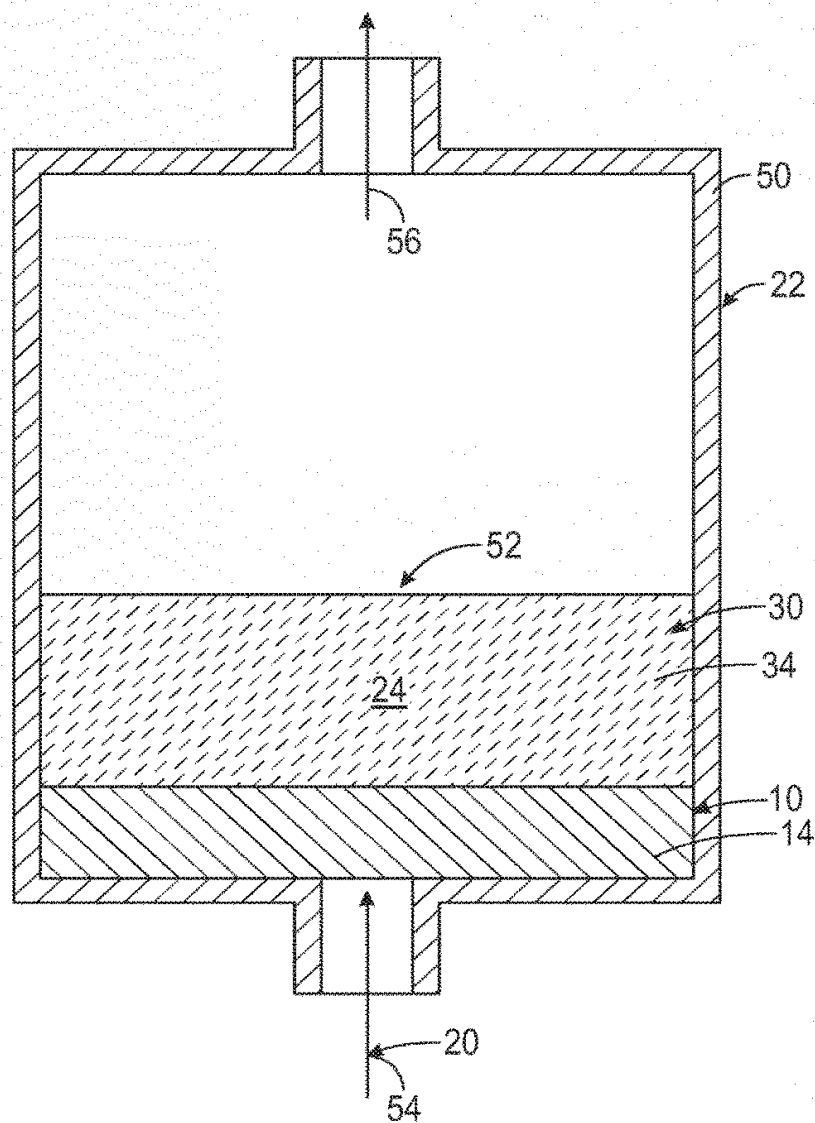
200

210 ─╮
┌───┐
│   Providing a Base Material Comprising a Metallic Compound │
└───┘
                              │
                              ▼
220 ─╮
┌───┐
│   Forming a Powder of the Base Material   │
└───┘
                              │
                              ▼
230 ─╮
┌───┐
│   Disposing the Base Powder Particles in a Reactor for   │
│   Reduction to Metallic Powder Particles   │
└───┘

FIG. 1

300

310 ─╮
┌───┐
│   Providing a Metallic Powder   │
└───┘
                              │
                              ▼
320 ─╮
┌───┐
│   Depositing a Nanoscale Metallic Coating Layer on Outer   │
│   Surfaces of the Metallic Powder Particles   │
└───┘
                              │
                              ▼
330 ─╮
┌───┐
│   Forming a Powder Metal Compact from the Coated   │
│   Metallic Powder Particles   │
└───┘

FIG. 2

FIG. 3

3/6

FIG. 4

FIG. 5

FIG. 6

100

17   18   16

14

12

FIG. 7

(54) Title: REALEASE ASSIST MICROCAPSULES

(57) Abstract

The invention is a microcapsule consisting of three components: 1) a shell or wall material layer (4); 2) a core material (3) consiting of an active ingredient; 3) a propellant (2) which is the second core material. The invention is a microcapsule (1) consisting of two core materials, one being an active core ingredient (3) while the other is a propellant (2), both surrounded by an encapsulating shell layer (4). The propellant (2) acts to either explode the capsule (1) or to help accelerate the release of the active core material (3) when the capsule is heated. The capsules have a triggered time release function, caused by heat acting upon the propellant core (2), which then acts to push more of the active ingredient (3) through the wall membrane of the capsule shell, or to explode the capsule from within.

ECOMETAL-002110

RELEASE ASSIST MICROCAPSULES

Field of Invention

5

This invention relates to an improved method of effecting the release of an active core from microcapsules.

10   Additionally this invention relates to encapsulated fungicides.

A further relationship exists to encapsulated catalysts.

There are four main release mechanisms for
15 microcapsules available. Conventional microcapsules release their active core material through:

1.   Diffusion of the active across the shell membrane

2.   Leakage of the active core through pores in
20 the structure of the microcapsule

3.   Interaction with another chemical, or solvent

4.   The use of a force which causes the capsule to break or dissolve.

25   A microcapsule may be classified as a either a Break On Demand or a Time Release product.

Time Release is a term used to describe a slow release over a period of time of the active core material from the confines of the capsule.

30   There are several problems with conventional Time Release microcapsules:

1.   They generally have a short shelf life period, often releasing the core too soon.

2.   Most such capsules generally have very fragile
35 shells, making them unsuitable to many industrial applications.

3.   They often have pre-mature chemical reactions with the environment they are placed in due to early release of the active core material from the capsule.

2

Break on Demand microcapsules are capsules which
generally have thicker shells, allowing little or no release
of the active core material until a physical force or
chemical reaction causes the shell to rupture. Such capsules
5 are virtually inert until an outside force effects the
breaking or dissolution of the shell.

The shelf life stability of microencapsulated chemicals
has inhibited the application of microencapsulation
technology to many fields. In many cases the Time Release
10 capsules release far too early. Using a Break On Demand
capsule system can often result in a capsule which does not
release at all. Examples of such problems can be found
through an examination of the encapsulation of catalysts and
fungicides:

15   **MILDEW SUPPRESSANT FUNGICIDES FOR PAINT USE**

In this project a fungicide is mixed into a can of
water based paint, the intent being to provide mildew
protection after a surface has been painted. The paint is
generally used in wet or damp environments. The fungicide is
20 intended to avoid discoloration of the painted surface. Most
fungicides available on the market react with the
ingredients in the paint or dissolve while the paint can is
stored on the shelf, a period of time which can last past
one full year. The shelf life reactivity problem leads to a
25 loss of potency for the fungicide. Encapsulation of the
fungicide, to avoid the chemical reaction problem, can
produce either a Reservoir capsule or a Micro-sponge
type capsule, a capsule with pores. The Micro-Sponge type
capsule allows the fungicide to leak from the capsule while
30 stored on the shelf, thereby having little protection for
the active material.

The Reservoir construction leads to a capsule with a
shell which is so thick as to not allow any leakage of the
active or diffusion to occur, avoiding premature reaction
35 during shelf storage, but the shell may also not allow
release after the surface has been painted either. In this

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application, where microencapsulation appears to be of
potential benefit the encapsulation effort is defeated
through shelf life and release difficulties.

ENCAPSULATED CATALYSTS

5   In this field microcapsules are intended as a means of
delivering a catalyst to a particular location or at a
particular time in a chemical process, without chemical
reaction along the way. Catalysts are isolated within a
capsule until the shell is broken of dissolved. Heat is
10 often used to melt away the capsule shell to release the
active catalyst material. In theory this should enable
satisfactory controlled delivery of a catalyst. In practice
however catalyst compounds often react with the shell
material, crosslinking the polymer. This can increase the
15 melt point of the shell material to a level higher than
desired or it can lead to a weakening of the shell itself,
producing cracks and lesions in the capsule wall. The
resultant capsules often have no longevity or actually do
not contain the original quality of catalyst. Using
20 substitute shell materials in the capsule construction,
shells which will not react with the catalyst, often produce
undesirable traits in the resulting product. An example
would be the encapsulation of Butyl Tuads, a common rubber
catalyst, which was desired to be released from the capsule
25 at temperatures below 100° (c). The chosen shell material,
which had a melt point of 65° (c) reacted with the catalyst
and would release only at 180° (c). An attempt was made to
use a non reactive second polymer which isolated the
catalyst properly, but had a temperature melt point of 250
30 (C). The problem was: How to get the catalyst to release in
a non-reactive shell at a temperature below 100 (C) ?
Conventional microcapsule release methods did not have a
suitable effect in this project.

        To solve these problems the use of a secured form of
35 reservoir microcapsule construction is employed, a capsule
which does not allow diffusion and does not have pores which

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would allow core leakage. Normally such Secured
Microcapsules do not have a Time Release Function. Instead
these capsules are usually employed in operations whereupon
a Break on Demand function is desired. In this instance the
5 Break on Demand capsule is caused to a have a time release
function by using a Triggered Release approach.

In this embodiment of the invention a propellant is
added to the core material to cause the active core to
release under certain conditions. The preferred condition is
10 to employ heat to cause the propellant to accelerate the
release of the active material. A propellant is placed along
with the active material as the core of the microcapsules.
When heat is applied the propellant can act to explode the
capsule from within, thus providing a burst release
15 function, OR the propellant can act to accelerate the
diffusion rate of the active by pushing the active material
through the pores in the capsule shell.

In the Fungicide example outlined above the use of a
Release Assist Approach was attempted whereby a solvent was
20 added to the fungicide core material and a Reservoir type
sealed capsule was produced around the combination core. The
resultant capsules exhibited a strong resistance to shelf
life deteriorate in the paint can. Later after the paint was
applied to a painted surface the capsules began to release.
25 In this case the painted surface was the exterior of a house
where the heat of sunlight acted to warm the capsules
within the paint layer. The heat caused the solvent within
the capsule to partially volatilize. The resulting vapors
produced a pressure within the capsules which then acted to
30 "push" the fungicide second core through the shell of the
capsule. This push is triggered by heat and acts to
accelerate the release of the capsule. By adjusting the
amount of solvent within the core the release rate after the
heat trigger can be controlled to take place over a series
35 of days or weeks.

In the catalyst example where the catalyst core reacted

with the shell of the capsule the release function
difficulties are solved by using a non-reactive polymer as
the capsule shell, together with a solvent as a second core.
The catalyst does not react with the new polymer but the
5 capsule normally has a melt point higher than desired. The
addition of the solvent solves this problem. By choosing a
solvent with a low enough boiling point the capsule can be
made to release at the desired temperature. When the capsule
is heated to the boiling point of the solvent second core,
10 the solvent volatilizes completely. The resultant gas then
exerts a pressure upon the interiorof the capsule, causing
the capsule to explode outward. The explosion occurs at a
temperature lower than that of the shell polymer, and closer
to the boiling point of the solvent. In this manner the
15 solvent acts as a propellant, providing a Burst Release of
the active material when the correct temperature level has
been obtained.

There are many applications in the prior art where
capsules are produced using a wide variety of techniques,
20 capsules which can have an enhanced release profile or
function using the Release Assist approaches defined in this
invention.

The present invention encompasses encapsulation of
substances in liquid, solid or slurry form. These substances
25 may be pharmaceutical agents, catalysts, fungicides,
pesticides or any other chemical. Encapsulating walls may or
may not be permeable to core material or other materials to
which the completed capsules may later be added. Capsules
provided by the present invention may be capable of slow
30 release mechanisms (commonly referred to as "time release")
or may be released in a sudden method caused by heat,
ultraviolet light, microwaves, ultrasonics or other energy
media or may be released through dissolution of the capsule
wall. In each instance of capsule release the release
35 function is aided by the use of a propellant material which
has been added to the active core material, whereby the

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propellant acts to accelerate the release of the
active.

    Accordingly , a first object of this invention is to
provide a microencapsulated product that possess a special
5 release function which may be either a Sudden or a Slow
release system which employs the use of a propellant or
solvent as an additive to the active core of said
microencapsulated product, whereby the release function of
the capsule is enhanced in some manner through the use of
10 the propellant additive.

    A second object of this invention is to enable Time
Release capsules to become stable during shelf storage,
beginning their time release function after that function
has been triggered by some effective means.

15   A third object of this invention is to enable
microencapsulated compounds to have a greater utility by
providing an expanded selection of polymers for use as
capsule wall materials, by enhancing the release function of
the resulting microencapsulated product.

20   A fourth object of the invention is to provide means of
encapsulating difficult or very active chemical compounds by
providing a different release mechanism, which in turn
provides a greater selection of encapsulating techniques and
technologies.

25   A fifth object of the invention is to provide a means
of fast release at narrow temperature ranges of a confined
active core from a microcapsule by providing a propellant
additive to the the active core material.

    Other objects and advantages of the present invention
30 will e obvious from the following descriptions, drawings
and experiments.

Brief Description Of The Drawings

    FIG. 1   is an illustration of the major capsule forms
available through conventional microencapsulation processes.
35   FIG. 2   is an illustration of the preferred
embodiment of the invention, a capsule containing a

propellant additive to the active core material.

　　　FIGS. 3 and 4 are graphs indicating the release
temperatures of a microcapsule containing a catalyst active
core material, mixed with a solvent, which acts as the
5 propellant.

　　　FIG. 5 is an illustration of one method usable to form
microcapsules, called Coacervation.

　　　TABLE 1 is an chart indicating the release rates of
capsules containing encapsulated Folpet compared to
10 capsules using the Release Assist enhancement as measured by
a per centage of weight loss over a period of time.

　　　TABLE 2 is a comparison of the release temperatures
of a catalyst known as Butyl Tuads which has been
encapsulated using a conventional reservoir type
15 construction vs. a release assist construction, whereupon
various solvents have been used as propellants.

　　　TABLE 3 is a list of potential polymers which may be
used as capsule shell materials.

　　　TABLE 4 is a chart indicating the bioactivity of
20 capsules containing a fungicide compared to capsules
containinga Release Assist mechanism employing a heat
sensitive propellant material as a second core.

Detailed Description Of The Invention

　　　FIG. 1 illustrates several conventional forms of
25 microcapsule construction. Each construction is capable of
enhanced release dynamics using this invention. In the first
example a Reservoir Capsule construction is indicated by a
egg type construction, characterized by a large amount of
core material surrounded by a single shell. The Micro-Sponge
30 construction is a capsule with a lower quantity of core
material embedded within many shell layers, allowing for a
slow release.

　　　The Multi-Wall capsule construction involves a
Reservoir type microcapsules with more than one shell layer.
35 The Multi-Core capsule is essentially a capsule, or several
smaller capsules, contained within a larger capsule.

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Each construction offer unique properties for
particular product applications. The normal release
mechanisms involve:

                    Slow dissolution of the shell layer
5   Permeation of the core active through the shell
                    Degradation of the shell due to heat, ultrasound,
microwave energy, pressure, impact, radiation, ultraviolet
light, solvent reactions or Ph adjustments

        FIG. 2 indicates the preferred embodiment of a Release
10 Assist capsule construction of the present invention 1 using
the Reservoir format, whereupon a phase change material or
propellant 2 has been added to the core material 3, both
contained by a shell layer 4.

        The illustrated capsule construction of the present
15 invention is a Reservoir type capsule. However, the present
invention may use any of the other capsule forms indicated
in FIG. 1.

        The embodiment of the invention shown in FIG. 2 is a
capsule 1 containing a shell 4 which surrounds a core
20 material combination consisting of a active ingredient 3
which is mixed with a propellant 2. The active 3 can be any
solid, liquid or slurry chemical compound. A partial list of
potential active's includes:

Pharmaceuticals	Pesticides
Catalysts	Fungicides
Fragrances	Emollients
Lubricants	Adhesives
Laundry additives	Bleaching agents
Dyes and Colorants	Essential Oils

30   A number of chemical compounds can be used as the
propellant 2 including:

Solvents	Phase Change Materials
Waxes	Peroxides
Propellants	Hydrocarbonous solutions
Water	Alcohols
Fuels	Gases

The propellant 2 may be any material which will
dissolve or expand, or convert into a gas when heat is
applied to the capsule 1. The action of the propellant 2
causes the Release Assist function of the invention to take
5 place, in that the propellant 2 acts to cause either a Burst
Release or an Accelerated Release or a Triggered Release
function to occur. The propellant may be in either solid,
liquid or gaseous form.

BURST RELEASE

10   The application of heat to the capsule 1 causes the
propellant 2 to expand within the capsule. This can cause
the shell 4 of the capsule 1 to elongate and expand beyond
the elastic limits of the polymer, eventually causing the
capsule to explode outward, providing a sudden or burst
15 release effect. The exploding action may be caused by a
propellant material 2 which expands under heat or phase
changes into a gaseous form during heating. The resulting
gas exerts a pressure against the interior of the shell 4
causing it to expand outward, eventually exploding the
20 capsule.

ACCELERATED RELEASE FUNCTION

The propellant 2 expands or phase changes with heat
application but does not generate enough force to actually
rupture the shell 4. Instead the pressure generated from the
25 expanding propellant 2 acts to accelerate the diffusion rate
of the active core 3 across the shell membrane 4. In most
capsules using a single shell reservoir type of construction
or a sponge type construction the active leaks from the
capsule through pores or cracks in the shell layer of the
30 capsule. Additionally the active core can diffuse across the
shell layer itself. In this application of the invention the
leakage rate or the diffusion rate is accelerated because of
a "push" exerted upon the active 3 by the expanding
propellant 2. The force of the expanding propellant or its
35 gaseous decomposition result can act to push the active 3
through pores in the capsule shell 4, at a rate faster than

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normal. Additionally the propellant under heat can act to
accelerate the diffusion rate of the active.

In this case heat acts as the trigger to cause the
accelerated release function to take place. By careful
5 choice of the propellant 2 the release function can be
controlled so as to only occur when heat is present. When
the heat is removed certain propellants 2 will coalesce back
into a neutral form, thereby slowing or ceasing the release
rate of the active 3, until heat is applied again. The
10 release function is triggered and controlled through the
application of heat to the capsule 1.

TRIGGERED RELEASE FUNCTION

Since the propellant acts by heat the capsules can be
made to have long shelf life stability. Normal time release
15 capsules frequently employ active diffusion functions or use
the sponge approach to allow a generous leakage rate from
the capsule. Sponge type capsules generally have very short
life spans. Diffusion capsules tend to have very thin
shells, thereby affecting their ability to resist stress.
20 Reservoir type capsules generally can be made with thicker
shells, allowing them to withstand higher degrees of shear
and industrial stress. However these type capsules have very
poor time release functions. Using the heat application to a
propellant core 2 can cause the release to become triggered
25 at a certain point, enhancing the shelf life stability of
the capsule product. Heat is used as the trigger, and can be
timed to occur at a specific point in a given process.

FIG. 3 is a temperature curve indicating the release
point of a microencapsulated capsule containing a catalyst –
30 solvent combination core. The catalyst is Butyl Tuads mixed
at 50% of the total core volume of the capsule .The solvent
is cyclohexane and causes the capsule to explode at a point
near the boiling point of the solvent. Cyclohexane was mixed
at 50% of the total core volume. In this case the shell
35 material was ureaformaldehyde which occupied 20 % of the
total volume of the capsule while the combination core

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materials occupied the remaining 80%. The graph is a
Differential Scanning Calorimetery test using a Dupont Model
2000 DSC device.

FIG. 4 is a graph illustrating the Thermogrimetric
5 Analysis of the same sample described in FIG. 3. Both graphs
indicate the point at which the capsule shell explodes,
indicated by a sharp peak in the temperature curve profile.
Through these graphs it can be seen that the capsules reach
a certain point whereupon the boiling solvent, cyclohexane,
10 causes the capsule to explode outward. In both thermal
studies the release point is comparable.

FIG. 5 is a illustration of the Coacervation method of
encapsulation, which was used in this particular series of
experiments. It should be noted that the Release assist
15 function can be duplicated through the use of a multitude of
encapsulation methods, systems, techniques and technologies
and the scope of this invention is not intended to be
limited by the use of just one such encapsulation process.
The Coacervation process is provided only as an example of a
20 encapsulation technique employed in the following
experiments.

TABLE 1 is a chart illustrating the release rates of
two samples of microencapsulated fungicides. The chart
illustrates the release rate of a conventionally
25 encapsulated fungicide known as Folpet when the capsule has
been immersed in water compared to the Release Assist
system of an enhanced encapsulated Folpet sample. The
Release Assist sample uses a propellant composed of
cyclohexane, an organic solvent, when heat is applied.

30   TABLE 2 is a table comparing the release results of a
particular test conducted using a conventional encapsulation
approach to a release assist approach using a common
chemical catalyst as the active core.

TABLE 3 is a listing of polymers known to be useful as
35 shell materials for microcapsules using the Release Assist
approach.

12

TABLE 3

Shell Formulations Are Fluid Film Formers

5
Including
• Solutions
• Melts
• Latexes

10
And May Be Hardened By
• Chemical Reaction
• Solvent Extraction
15
• Solvent Evaporation
or   • Combinations

Some Microencapsulation Matrix And Wall Chemicals

20
Natural Polymers

Carboxymethylcellose	Zein
Cellulose acetate phthalate	Nitrocellulose
Ethylcellulose	Propylhydroxylcellulose
Gelatin	Shellac
Gum Arabic	Succinylated gelatin
Starch	Waxes, paraffin
Bark	Proteins
Methylcellulose	Kraft lignin
Arabinogelactan	Natural Rubber

Synthetic Polymers

Polyvinyl alcohol	Polyvinylidene chloride
Polyethylene	Polyvinyl chloride
Polypropylene	Polyacrylate
Polystyrene	Polyacrylonitrile
Polyacrylamide	Chlorinated polyethylene
Polyether	Acetal copolymer
Polyester	Polyurethane
Polyamide	Polyvinylpyrrolidone
Polyurea	Poly (p-xyiylene)
Epoxy	Polymethyl methacrylate
Ethylene-vinyl acetate copolymer	Polyhydroxyethyl methacrylate
Polyvinyl acetate	

Synthetic Elastomers

Poly butadiene	Acrylonitrile
Polyisoprene	Nitrile
Neoprene	Butyl rubber
Chloroprene	Polysiloxane
Styrene-butadiene rubber	Hycrin rubber
Silicone rubber	Ethylene-propylene-diene copolymer

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TABLE 4　is a chart describing a test involving various
Fungi whereupon a encapsulated fungicide was used in an
effort to test boiactivity effects upon the target fungi. In
5 one test capsules containing a given fungicide, known as
Folpet, were made by conventional encapsulation techniques
as taught by Noren in the article, Investigation of
Microencapsulated Fungicides for use in Exterior Trade Sales
Paints, Vol 58, No. 734, March 1986 of the Journal of
10 Coatings Technology. These capsules, called Batch 1 on the
chart, were then compared to capsules made in the same
manner, except that a propellant was added to the core
material, ascribing to the teachings of this invention, and
indicated on the chart as Batch 2.

15 **TABLE 4**

FUNGAL RESISTANCE TO AQUEOUS PAINT FILMS CONTAINING
ENCAPSULATED FUNGICIDE, WITH SAMPLES BEING SUBJECTED TO
ARTIFICIAL "SUN LAMP" HEAT TO 90 (F) FOR 30 DAYS AFTER
SURFACE WAS COATED
20

FUNGI TYPE ASSIST	RAW FUNGICIDE	BATCH 1 ENCAPSULATED FUNGICIDE	BATCH 2 RELEASE FUNGICIDE
MIXED	10	9	3
PENICILLIUM FUNICULOSM	10	9	4
ASPERGILLUS NIGER	10	8	1
GLIOCLADIUM VIRENS	10	8	4

SCALE :　Growth Rate scale of 10 to 0 where 10
corresponds to complete coverage of the surface of the

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coated film. Lower number indicates reduced Fungi growth
activity , and greater efficiency for the fungicide. The Raw
fungicide was used as the standard.

Fungicide Used was known as Folpet, supplied by Nuodex
5 Inc., A standard loading of 40 % in latex paint was used.
Samples had been aged for 4 weeks prior to the test.

Results indicate that the encapsulated fungicide does
not have a significant effect. The Release Assist capsules,
under heat, however did provide decreased bioactivity for
10 the fungi.

In Table 4 it can be seen that the Batch 2 capsules
remained stable until heat was applied to them. At this
point the release function was triggered as the propellant
inside the capsule began to expand, pushing the fungicide
15 through cracks which developed in the expanding shell layer.

EXAMPLE 1

INCREASED SHELF LIFE STABILITY AND ACCELERATED RELEASE
THROUGH THE USE OF A RELEASE ASSIST CAPSULE CONSTRUCTION
USING A THERMAL TRIGGER TO INITIATE TIME RELEASE FUNCTION
20   A fungicide known as Folpet, obtained from Nuodex
Corporation, was encapsulated using the Coacervation
procedure using a urea-formaldehyde polymer as the shell
layer.

A second microcapsule batch was produced using the same
25 coacervation procedure, the same shell and the Folpet
active, but with a second core consisting of a solvent known
as Cyclohexane.

The two capsules were then compared for shelf life
stability, bio-activity upon release, and release
30 effectiveness.

The procedure used to produce the capsules was:

A pre-condensate of urea - formaldehyde resin was first
formed using 120 grams of urea mixed with 325 grams of 37%
aqueous formaldehyde containing 15 % methyl alcohol at room
35 temperature. Triethanolamine was added , one drop at a time,
to adjust the pH to 8. After 1 hour of agitation , 600 ml of

15

distilled water was added to the mixture, at room
temperature. Then, 130.5 grams of the pre-condensate was
further diluted with 200 ml of distilled water, producing a
final polymeric solution to be used as the shell layer.

5   Next 10 grams of the above described urea-formaldehyde
shell solution was mixed with 40 grams of Folpet fungicide
supplied by Nuodex Corporation, in 400 ml of water, for 60
minutes, at a temperature of 25 (c), under rapid agitation.
        At the end of the 60 minute period the heat was removed
10 to allow the mixture to cool back to room temperature, while
the agitation was maintained. Hydrochloric acid was added to
the mixture to adjust the Ph to slightly less than 6. Once
the Ph level had been obtained the mixture was allowed to
air cool for another 2 hours under moderate agitation.
15 Capsules were formed during this procedure and hardened by
the Ph adjustment into a solidified form. The capsules were
then filtered from the liquid mixture and examined. The
capsules contained approximately a 25% shell volume, and
were of the Reservoir type construction.
20   The capsules were then allowed to air dry for 5 days,
after which 20 grams of the completed capsules were then
immersed in a beaker of water containing 400 ml of tap
water. The capsules were then observed for release rate
activity over a period of 30 days, by testing the amount of
25 Ph change and conductivity change of the tap water over the
30 day period of time, in daily intervals. The capsules were
weighed prior to immersion. The weight was then periodically
checked to determine the loss rate over the test period.
Additionally some of the capsules were subjected to fungi
30 for tests of bioactivity.
        Another batch of microcapsules were produced using the
same ingredients and procedures listed above except that a
second core material was added to the reaction. The second
material was a solvent known as cyclohexane, which was
35 applied at a ratio of 20 % of the overall core material.
Folpet occupied 80 % of the resulting capsules while

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cyclohexane occupied approximately 20%. In this batch
however 40 grams of urea-formaldehyde resin instead of 10
grams was used in the final capsule mixture.

    The second batch of capsules were well formed, having a
5 Reservoir type construction, and size approximating the
first batch, from 5 to 30 microns. The second batch was
then filtered and tested using the same described
procedures. This batch was the release assist sample, and
contained a thicker shell than the first batch.

10   The capsules released at varying rates. TABLE 1
(A and B) illustrates the release rate over the 30 day
period for Batch 1 (coacervated Folpet) and Batch 2
(Coacervated Folpet/Cyclohexane). It can be seen that Batch
1 releases very quickly compared to Batch 2, which is the
15 Release Assist capsule product form of this invention.

TABLE 1 A

WEIGHT LOSS OF ENCAPSULATED FUNGICIDE SAMPLES, WHEN IMMERSED
IN TAP WATER, OVER 30 DAY PERIOD, AT   ROOM   TEMPERATURE
20

NO OF DAYS	BATCH 1 WEIGHT LOSS	BATCH 2 WEIGHT LOSS
25 0	0 %	0 %
5	2 %	0 %
30 10	16 %	0 %
15	24 %	0.50 %
35 20	72 %	0.65 %

40

17

NO OF DAYS	BATCH 1 WEIGHT LOSS	BATCH 2 WEIGHT LOSS
25	85 %	0.76 %
30	92 %	1.0 %

BATCH 1 = Encapsulated Folpet fungicide, reservoir
type construction using 15% shell (Urea-formaldehyde resin),
85% active core material, encapsulated through coacervation
procedure (interfacial polymerization technique), a
conventional encapsulation product.

BATCH 2 = Encapsulated Folpet using a reservoir
type capsule construction using 25% shell (Urea-formaldehyde
resin) 75% total core of which 50% is Folpet active and 50%
is cyclohexane solvent acting as a propellant.

BATCH 2 had a thicker shell and thereby had a greater
shelf life.

TABLE 1 B

RELEASE RATE OF ENCAPSULATED FOLPET FUNGICIDE WHEN
SAMPLE IS SUBJECTED TO HEAT OVER A THIRTY DAY PERIOD
TEMPERATURE LEVEL: 90 (F)

NO. OF DAYS	BATCH 1	BATCH 2
0	0 %	0 %
5	0 %	2 %
10	0 %	3.5 %
15	0 %	4.70 %
20	0 %	6.25 %

18

NO. OF DAYS	BATCH 1	BATCH 2
5 25	0 %	9.75 %
30	0 %	13.00 %

10   NOTE: BATCH 1 did not release at all during the 30 day trial period. BATCH 2 slowly released as the propellant (Cyclohexane) phase changed and produced a gas which exerted pressure against the interior surface of the capsule shell. The pressure caused cracks and lesions to form in the 15 capsule shell, through which the active fungicide could escape, yet the release rate was over a prolonged period of time.

     Even though the urea-formaldehyde resin was supposed to be a water barrier for the microcapsule the Folpet active 20 managed to diffuse or leak from the capsule. Folpet is a commonly used fungicide for mildew suppression in household paints. This test revealed that the product would have released slowly in the paint can during shelf storage, having no remaining potency after the paint had been applied 25 to its target surface. Indeed further examination of the data corresponded with a test conducted by Desoto Paints on encapsulated Folpet listed in the reference section of this application. The tests conducted by Desoto also indicated poor performance for the encapsulated Folpet.

30   Batch 2 had virtually no effective release over the 30 day period, loosing less than 1 % of its weight over the period compared with nearly a 92 % loss rate for the conventionally made capsules. Over a year long period the Batch 1 would have leached all of its active from the 35 capsule and would thereby become totally useless by the time it was applied as part of a paint coating to a given surface. Batch 2 would loose less than 12% of its weight by then however, providing approximately 88% active still

remaining within the sealed capsule (assuming that none of
the shell degraded within the liquid) These tests were
conducted with the application of water based paints in
mind.

5   In the bioactivity test the results wereremarkably
different. Both capsule batches showed no reaction when
exposed to Penicillium Funiculosm; Aspergillus Niger;
Gliocladium Virens fungi and a mixture of the three at room
temperature. But when "sunlight" exposures were made,
10 whereupon the capsules were subjected to the target fungi
under a heat lamp, which approximates a temperature of 85
(f), the true differences in the batches presented
themselves. Batch 1 showed little or no effective reaction.
Batch 2, containing the Release Assist construction, showed
15 a marked ability to kill the fungi. It is suggested by the
inventor that the heat of the lamp caused the cyclohexane
second core of the capsules of Batch number 2 to volatilize.
This generated an internal pressure within the capsules and
this then acted to "push" the Folpet active fungicide
20 through pores in the capsule shell which had developed
during immersion in the water. This "push" action acted to
accelerate the release function, after shelf storage while
the capsules were immersed in water, and after the heat
trigger was applied by the heat lamp. Batch two was observed
25 for another 30 days to still be effective in destroying the
target fungi, indicating that the "push" effect was not a
sudden effective release, but a prolonged release over a
period of time.
        Table 4 indicates the bioactivity results of the above
30 example. Observation of the painted surfaces revealed that
niether capsule system had broken. The coacervated sample
with no solvent core, Batch 1 had remained intact with no
release at all. Batch 2, the Release Assist capsules, had
not exploded or completly broken but photographic analysis
35 revealed that there were several cracks and pores in the
surface of the capsule, which had not been present when the

capsules were first made. The cracks and pores in the shell
of the capsule were the result of the heating activity,
whereupon the expanding propellant forced the fungicide
through the weak spots in the capsule construction.

5   **EXAMPLE 2**

SUDDEN (EXPLOSIVE) RELEASE THROUGH A THERMAL
TRIGGERING OF A RELEASE ASSIST MICROCAPSULE

A batch of Urea-formaldehyde resin was made according
to the procedure outline in Example 1 above. In this
10 experiment 40 grams of a chemical catalyst known as Butyl
Tuads was added to the reaction vessel instead of the Folpet
material used in Example 1. The encapsulation procedure was
the same. Capsules were produced at approximately 50 - 100
microns with a Reservoir type construction. These capsules
15 were then filtered from the mixture and allowed to air dry
for 24 hours.

A second bath was produced using the Release Assist
approach whereupon a solvent was added to the capsule as the
second core material. The solvent was added at differing
20 quantities as a ratio of the active catalyst to the solvent.
The shell layer remained at a constant 20% of the volume of
the overall capsule in each formulation tested. Differing
solvents were used to obtain a wide variety of Release
points.

25   Each capsule batch produced was subjected to a Heat
Stage device to measure the point at which the capsule shell
melted under heat. The rupturing of the capsule was observed
visually under a magnifying lens attached to the heat stage
device. In each instance where a solvent was employed as a
30 second core, the capsules were observed to explode when heat
was applied to the capsule unit. The capsules which
contained no solvent slowly melted as heat was applied
whereas the solvent filled capsules tended to expand in size
and then explode.

35   The samples were then subjected to DSC (differential
scanning calorimetry) and TGA (thermogravimetric

analysis) tests to determine the temperature profiles of
each sample. The results are shown in TABLE 2:

TABLE 2

BATCH NO.	SHELL TYPE	SOLVENT NAME	CORE %	BOIL. POINT	CAPSULES SIZE (AVG)	RELEASE TEMP.
2A (c)	U/F	NONE	0	----	250	255
2B (c)	U/F	TOL.	50	111 (c)	200	180
2C * (c)	U/F	CYC.	50	81 (c)	150	160
2D (c)	U/F	HEX.	50	69 (c)	100	196
2E (c)	U/F	CYC.	40	81 (c)	100	202

TOL. = TOLUENE   CYC. = CYCLOHEXANE   HEX. = HEXANE

RELEASE TEMP. = THE RELEASE TEMPERATURE OF THE CAPSULE

U/F = UREA-FORMALDEHYDE RESIN SHELL

In sample 2A the capsule was observed to release
through a Melting of the shell. The shell began a slow
degradation as heat was applied to the capsule.

Sample 2C contained a capsule shell which had not been
crosslinked into a hardened form, enabling the vololizing
sovent to break the weaker shell. The other samples were
crosslinked into a harder shell formation by adjusting the
Ph to a lower level during the final polmerization stage of
the resin based shell. It is apparent from these tests that
the strength of the shell layer is a factor in achieving the
desired release temperature. If the capsule shell is very
thick the strength of the wall membrane is sufficient to
resist the expansion force exerted upon it from within the
capsule by the gases emitted from the volotilizing
propellant or solvent second core. Likewise if the shell is
hardened through a polymerization or other strenghtening

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process it may also raise the release temperature of the capsule.

The temperature profiles indicated in the release curves of FIG. 3 and FIG. 4, developed by a Differential
5 Scanning Calorimeter and Thermogravimetric Analysis   device manufactured by E.I. Du Pont De Nemours Instruments Division, Model 2000, indicate the release temperature of Sample 2 E.

In Examples 2B,2C,2D,2E, the capsules exploded when
10 they were heated to the indicated release temperature. The release was sudden and complete, in a burst effect which not only destroyed the capsule shell but actually expelled the active core from the catalyst.

In this example it can be seen that the solvent acts as
15 a propellant to explode the shell of the capsule at temperatures lower than the normally melt point of the polymer used in the capsules. In each case the solvent acted to lower the release temperature of the capsule. Additionally the solvent acted to explode the capsules at a
20 very precise release point as opposed to an extended release over a period of time. The solvent provided for a sudden burst release. For each sample the solvents vaporization tended to expel or throw the active material from the capsule once the capsule was broken. Heat is used as the
25 release trigger but the temperature at which the capsule ruptures can be adjusted through the choice of the solvent used and the percentage of solvent used in the capsule as opposed to the percentage of active core.

In the above examples several functions of the
30 invention have been described. The invention provides for a propellant compound to be added to the active core of a microcapsule whereupon the resultant capsule product will provide the following functions:

1.   Enable a microcapsule to have a thicker shell
35 construction so as to provide an extended shelf life for the product.

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2.   Enable the sudden release of a microcapsule at a specific temperature level.

3.   Enable the acceleration of a active core material through pores or lesions in the capsule shell layer after a
5 thermal trigger has been applied to the capsule.

4.   Increase the diffusion rate of of an active core across a shell membrane after a thermal trigger has been applied.

5.   Enable shell to core incompatibility problems to
10 be solved be allowing the use of compatible shell polymers, with adjusted release points through the use of a propellant as a second core to the capsule.

6.   Allow for exploding capsules through the use of a propellant second core, which when heated will cause a rapid
15 rupture of the shell layer and a expulsion of the active core from the confines of the capsule.   •

In the above examples a batch process was employed using Coacervation to produce Reservoir type microcapsules. The invention may also be practiced using any other form of
20 capsule construction including but not limited to Micro-sponge or entrapment capsules, multi-wall capsules or multi-core capsules. The invention may also be practiced using any other form of capsule manufacture process including but not limited to Coacervation, Thermal
25 Coacervation, Interfacial Polymerization Solvent Evaporation or any mechanical means.

While the invention has been described with respect to specific embodiments, it is understood that variations are possible. The examples given are intended to be
30 illustrative, and not limiting. These and other variations of the invention should be deemed within the spirit and scope of the following claims:

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What is claimed is:

     1.   A microcapsule which comprises: a first core material, and a second core material, said second core material having the property of causing the release of said
5 first core material when heat is applied to the capsule.

     2.   The microcapsule of claim 1, wherein said first and second core materials are encompassed by a shell, said second core material causing said shell to loose its structural integrity when said heat is applied to the
10 microcapsule, thereby permitting the release of said first core material.

     3.   The microcapsule of claim 2, wherein the loss of structural integrity of said shell is caused by the volatilization of said second core material due to said
15 heat.

     4.   The microcapsule of claim 3, wherein said volatilization of said second core material causes said first core material to diffuse through said shell.

     5.   The microcapsule of claim 3, wherein said shell
20 has openings therein and wherein said volatilization of said second core material causes said first core material to be forced through said openings in said shell.

     6.   The microcapsule of claim 3, wherein said volatilization of said second core material is rapid,
25 thereby causing said shell to burst.

     7.   The microcapsule of claim 1, 2, 3, 4, 5, or 6 wherein said first core material is a biocide selected from the group consisting of fungicides, bactericides, and pesticides.

30   8.   The microcapsule of claim 1, 2, 3, 4, 5, or 6 wherein said first core material is a catalyst.

RESERVOIR CAPSULE: SINGLE FILL
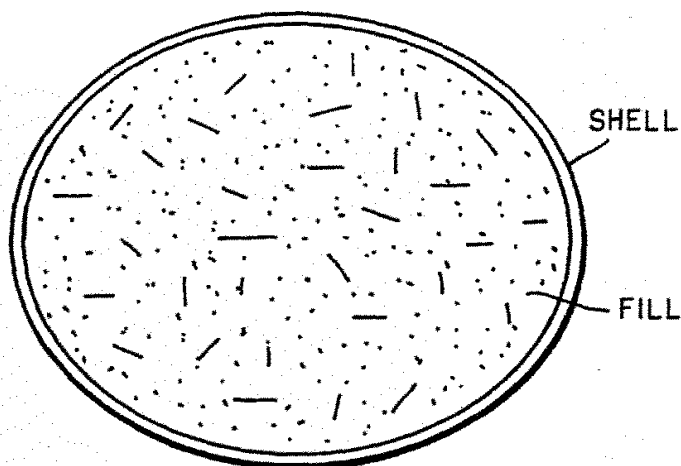
SHELL

FILL

FIG. 1A

MICRO-SPONGE CAPSULE

SHELL LAYERS

FILL DROPLET
OR PARTICLE

PORE OPENINGS
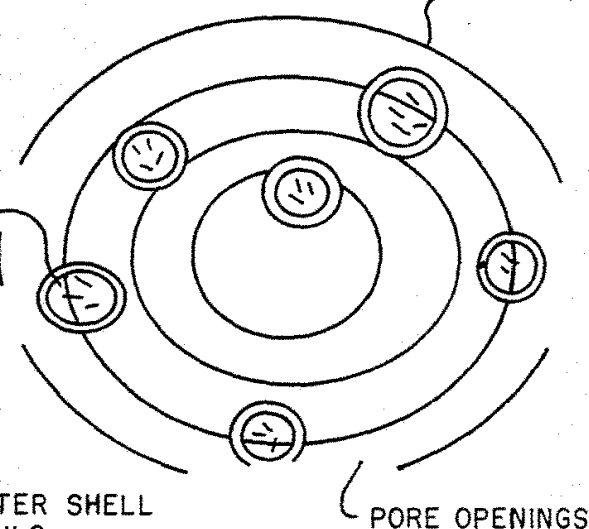
FIG. 1B

MULTI-FILL CAPSULE: CAPSULES
WITHIN CAPSULES

OUTER SHELL
#2

OUTER
FILL #2

INNER FILL #1

INNER SHELL
#1
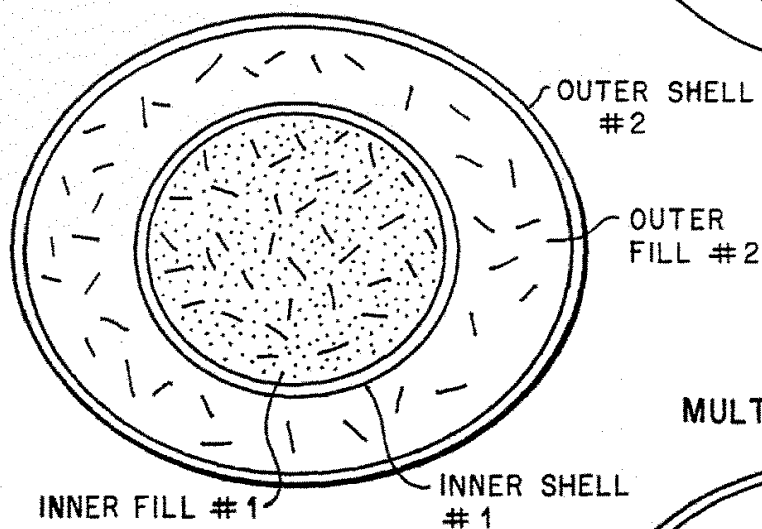
FIG. 1C
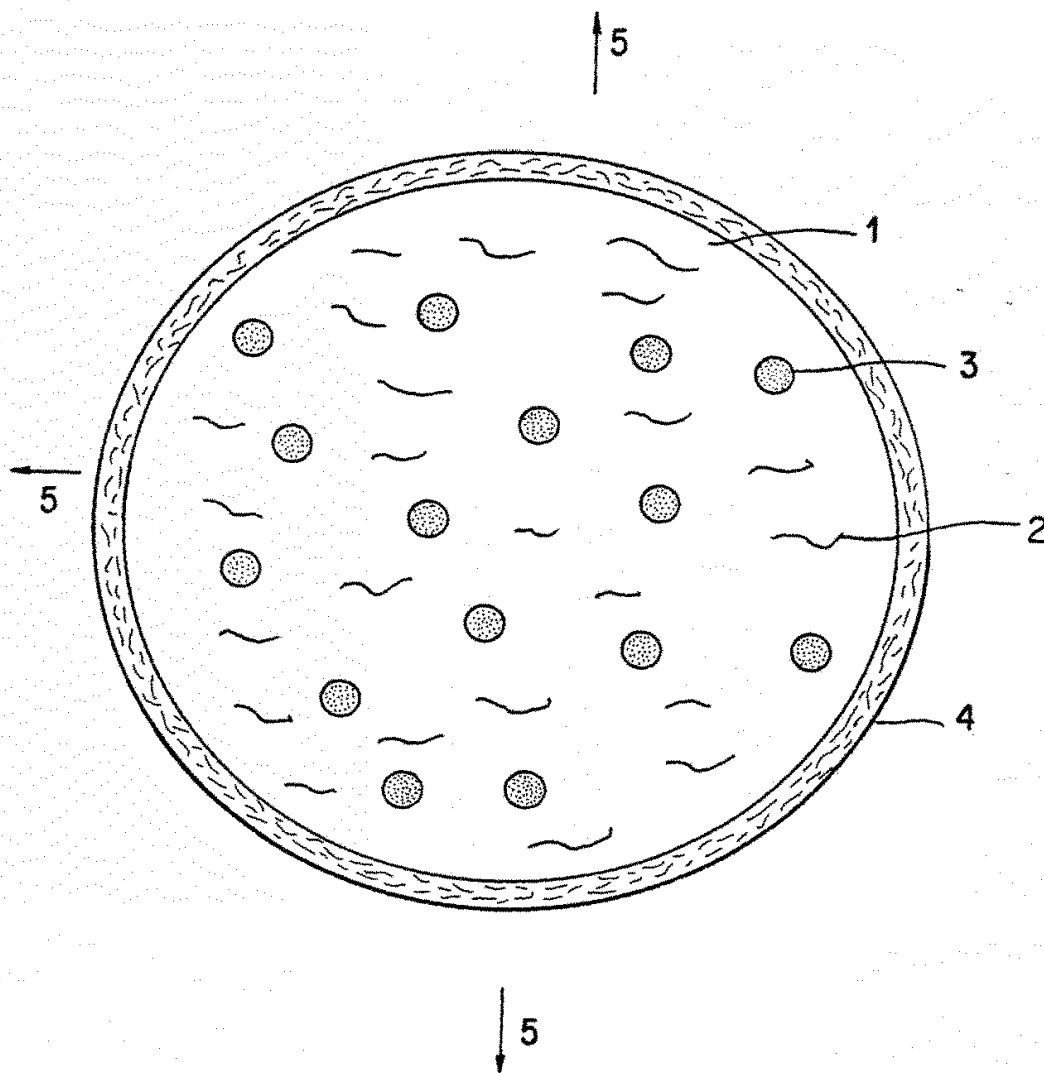
MULTI-WALL CAPSULES

FILL

MULTIPLE
SHELL LAYERS
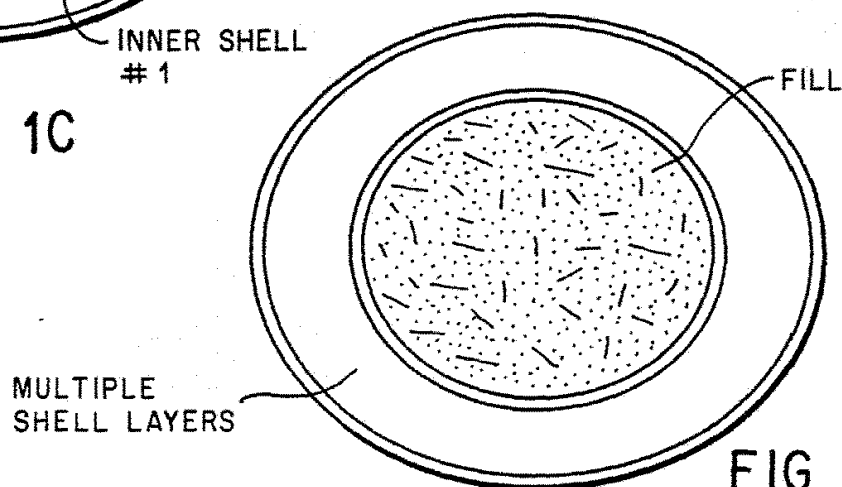
FIG. 1D

FIG. 2

SAMPLE: AES-34
SIZE: 2.7220 mg
METHOD: A - 600° @ 10°/MIN
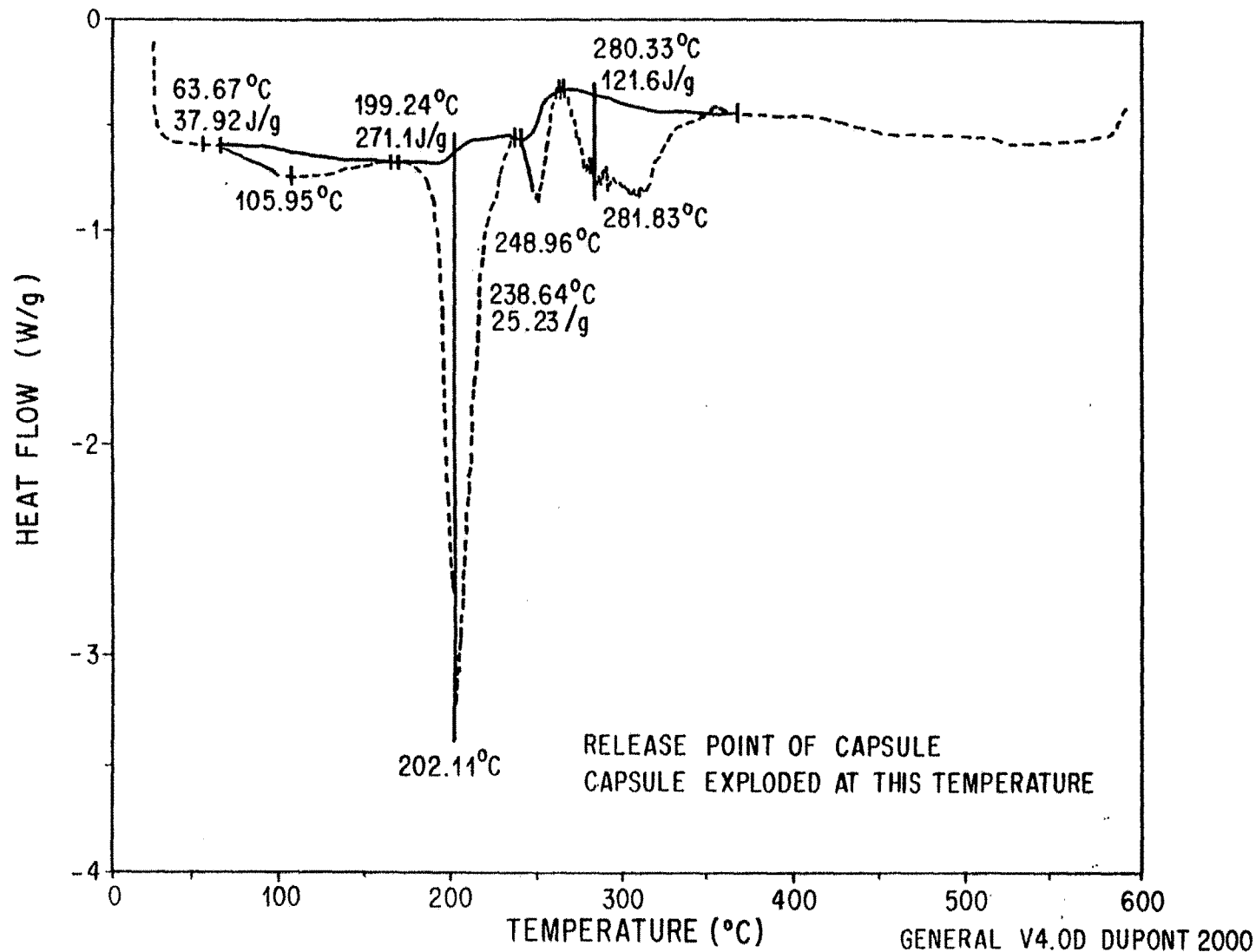COMMENT: APPROXIMATELY 50CC/MIN NITROGEN

DSC

FILE: ESI.05
OPERATOR: JHF
RUN DATE: 17 - AUG - 88 14:57

63.67°C
37.92 J/g

105.95°C

199.24°C
271.1 J/g

280.33°C
121.6 J/g

281.83°C

248.96°C

238.64°C
25.23/g

202.11°C

RELEASE POINT OF CAPSULE
CAPSULE EXPLODED AT THIS TEMPERATURE

HEAT FLOW (W/g)

TEMPERATURE (°C)

GENERAL V4.0D DUPONT 2000

FIG. 3

3/5

ECOMETAL-002137

FIG. 4

COACERVATION

FIG. 5

(54)MAGNESIUM ALLOY WITH HEAT RESISTANCE AND FLAME RETARDANCY, AND METHOD OF MANUFACTURING THE SAME

(57)Abstract

PROBLEM TO BE SOLVED: To provide a magnesium alloy with heat resistance and flame retardancy usable under a high temperature environment, and a method of manufacturing the same.

SOLUTION: The magnesium alloy 10 contains 0.5-5 mass% Ca and 0.5-5 mass% Si, and a CaMgSi phase 12 is crystallized in a Mg phase 11 serving as a parent phase, thereby providing the heat resistance. The method of manufacturing the magnesium alloy 10 includes the steps of: heating a Mg alloy raw material in a molten state sequentially added with Ca and Si in a temperature range of 800-900° C and then solidifying the same; and crystallizing the CaMgSi phase 12 in the Mg phase 11 serving as the parent phase, thereby providing the heat resistance.

CLAIMS

[Claim(s)]

[Claim 1]

A Magnesium alloy which has heat resistance and fire retardancy having made a CaMgSi phase crystallize and making heat resistance have into Mg phase which 0.5-5 mass % Has the 0.5 to 5 mass %, and Si, and turns into [Si] a host phase in Ca.

[Claim 2]

A Magnesium alloy which has heat resistance and fire retardancy having made a grain boundary of the aforementioned Mg phase crystallize an Al_2Ca phase further, and improving hardness to it in a Magnesium alloy which has heat resistance according to claim 1 and fire retardancy.

[Claim 3]

A Magnesium alloy which has heat resistance and fire retardancy having made $Mg_2 Si$ phase crystallize further and improving creep resistance in the aforementioned Mg phase in a Magnesium alloy which has heat resistance according to claim 1 or 2 and fire retardancy.

[Claim 4]

It is a manufacturing method of a Magnesium alloy which has heat resistance according to claim 1 and fire retardancy, A manufacturing method of a Magnesium alloy which has heat resistance and fire retardancy making it solidify after Ca and Si heat a Mg-alloy raw material of a molten state added sequentially in an 800-900 degrees C temperature requirement, making the aforementioned CaMgSi phase crystallize and making heat resistance have into the aforementioned Mg phase.

[Claim 5]

In a manufacturing method of a Magnesium alloy which has heat resistance according to claim 4 and fire retardancy, While heating the aforementioned Mg-alloy raw material made to crystallize the aforementioned CaMgSi phase in a 600-800 degrees C

ECOMETAL-002141

temperature requirement, A manufacturing method of a Magnesium alloy which has heat resistance and fire retardancy adding Ca further in the Mg-alloy raw material, solidifying the Mg-alloy raw material, making a grain boundary of the aforementioned Mg phase crystallize an Al_2Ca phase, and improving hardness.

[Claim 6]

In a manufacturing method of a Magnesium alloy which has heat resistance according to claim 4 or 5 and fire retardancy, While heating the aforementioned Mg-alloy raw material made to crystallize the aforementioned CaMgSi phase, A manufacturing method of a Magnesium alloy which has heat resistance and fire retardancy adding Si further in the Mg-alloy raw material, solidifying the Mg-alloy raw material, making Mg_2 Si phase crystallize in the aforementioned Mg phase, and improving creep resistance.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

The present invention relates to a Magnesium alloy which has heat resistance and fire retardancy suitable for the use under hot environments, and a manufacturing method for the same.

[Background of the Invention]

[0002]

In recent years, in the automobile industrial world, although improvement in the further fuel consumption, vibration and reduction of noise, etc. are called for, the form of an aluminum alloy and material development which are used for the engine material of an automobile already mature, and cannot expect the further advanced features, for example.

As a means to cope with this problem effectively, it is light into engine material as compared with an aluminum alloy, and reactivity with iron is low, and it considers using the Magnesium alloy which has still higher vibration attenuation performance. By this, a weight saving, friction, and reduction of printing can be aimed at, and fuel consumption can be improved, and vibration and noise can also be reduced.

[0003]

However, the strength of the Magnesium alloy in the elevated temperature was low, and since it was a material which results in combustion when temperature rises, it did not fit the material used under hot environments like engine material.

Then, for example, the Magnesium alloy made into fire retardancy was proposed by the Patent document 1 by adding Ca in a raw material (for example, see Patent Document 1).

[Citation list]

[Patent literature]

[0004]

[Patent document 1] Japanese Patent No. 3318606 gazette

[Summary of Invention]

[Problem to be solved by the invention]

[0005]

Although the Magnesium alloy in which Ca was added could go up the hardness of the Magnesium alloy as compared with the case where Ca is not added and it also had heat resistance, it did not have sufficient heat resistance of the degree which can be used

under an elevated-temperature situation (for example, 200 degrees C or more) like the engine material of an automobile.

[0006]

The present invention was made in view of this situation, and an object of the present invention is to provide a Magnesium alloy which has usable heat resistance and fire retardancy under hot environments, and a manufacturing method for the same.

[Means for solving problem]

[0007]

The Magnesium alloy which has the heat resistance and fire retardancy concerning first invention in alignment with the aforementioned object made the CaMgSi phase crystallize, and made heat resistance have into Mg phase which 0.5-5 mass % Has the 0.5 to 5 mass %, and Si, and turns into [Si] a host phase in Ca.

[0008]

In the Magnesium alloy which has the heat resistance and fire retardancy concerning first invention, it is preferable to make the grain boundary of the aforementioned Mg phase crystallize an Al$_2$Ca phase further, and to improve hardness to it.

[0009]

In the Magnesium alloy which has the heat resistance and fire retardancy concerning first invention, in the aforementioned Mg phase, Mg$_2$ Si phase may be made to crystallize further and creep resistance may be improved.

[0010]

The manufacturing method of the Magnesium alloy which has the heat resistance and fire retardancy concerning second invention in alignment with the aforementioned object, Are a manufacturing method of the Magnesium alloy which has the heat resistance and fire retardancy concerning first invention, after Ca and Si heat the Mg-alloy raw material of the molten state added sequentially in an 800-900 degrees C temperature requirement, it is made to solidify, and the aforementioned CaMgSi phase is made to crystallize and heat resistance is made to have into the aforementioned Mg phase.

[0011]

In the manufacturing method of the Magnesium alloy which has the heat resistance and fire retardancy concerning second invention, It is preferable to add Ca further in the Mg-alloy raw material, to solidify the Mg-alloy raw material, to make the grain boundary of the aforementioned Mg phase crystallize an Al$_2$Ca phase, and to improve hardness, heating the aforementioned Mg-alloy raw material made to crystallize the aforementioned CaMgSi phase in a 600-800 degrees C temperature requirement.

[0012]

In the manufacturing method of the Magnesium alloy which has the heat resistance and fire retardancy concerning second invention, Heating the aforementioned Mg-alloy raw material made to crystallize the aforementioned CaMgSi phase, Si is further added in the Mg-alloy raw material, the Mg-alloy raw material is solidified, in the aforementioned Mg phase, Mg_2 Si phase may be made to crystallize and creep resistance may be improved.

[Effect of the Invention]

[0013]

Since a Magnesium alloy which has the heat resistance and fire retardancy concerning the present invention, and a manufacturing method for the same are making the CaMgSi phase crystallize in Mg phase used as a host phase, they can comprise heat resistance. A CaMgSi phase is hard, and is a high-melting point, and this is because it excels in heat resistance.

Thus, since a Magnesium alloy is provided with heat resistance, it can be used under hot environments and can aim at expansion of a use purpose.

[0014]

When the grain boundary of Mg phase of a Magnesium alloy is made to crystallize an Al_2Ca phase further, the hardness of a Magnesium alloy can be improved. An Al_2Ca phase is hard, and is a high-melting point, and this is because it has heat resistance.

Therefore, according to the synergistic effect of a CaMgSi phase and an Al_2Ca phase, further improvement in the hardness of a Magnesium alloy can be aimed at, and heat resistance can also be improved sufficiently.

[0015]

And when Mg_2 Si phase is made to crystallize further in Mg phase of a Magnesium alloy, the creep resistance of a Magnesium alloy can be improved.

Therefore, further expansion of the use purpose of a Magnesium alloy can be aimed at.

[Brief Description of the Drawings]

[0016]

[Drawing 1]It is a mimetic diagram of the organization of a Magnesium alloy which has the heat resistance and fire retardancy concerning the 1 embodiment of the present invention.

[Drawing 2]Temperature is an explanatory view showing the influence which it has on the tensile strength of a Magnesium alloy.

[Description of Embodiments]

[0017]

Then, referring to the attached Drawings, it describes per embodiment which materialized the present invention, and presents an understanding of the present invention.

As shown in Fig.1, Magnesium alloy (henceforth a Mg alloy) 10 which has the heat resistance and fire retardancy concerning the 1 embodiment of the present invention, By structure control, make the CaMgSi phase 12 crystallize, and heat resistance is made to have into the alphaMg (alpha magnesium) phase 11 used as a host phase (it is also called a base metal), for example, it is suitable for the use under hot environments like the engine material of an automobile. Hereinafter, it describes in detail.

[0018]

Ca (calcium) and Si (silicon) are further added by the Mg-Al-Zn system alloy in which Mg alloy 10 has Mg (magnesium), Al (aluminum), Zn (zinc), and Mn (manganese). Mg is specifically made into a subject (more than the 80 mass %), and Al is the one to 15 mass % (here 12 mass %). The 0.1 to 5 mass % (here 0.7 mass %) and Mn constitute Ca from the 0.1 to 2 mass % (here 0.3 mass %), it comprises the 0.5 to 5 mass % (here 1 mass %), and Si comprises the 0.5 to 5 mass % (here 1 mass %), and inevitable impurities for Zn.

[0019]

If Ca and Si are contained in order for a Mg alloy to make a CaMgSi phase crystallize in Mg phase (especially alphaMg phase) used as a host phase, the amount of each of Al in a Mg alloy, Zn, and Mn will not be limited to the above-mentioned value. Ca and Si can also be added into alloys, such as Mg single entity, a Mg-Al system, a Mg-Mn system, a Mg-Zn system, and a Mg-Zn-Zr system, for example. The element of others [Mg alloy], for example, Sr (strontium), Be (beryllium), Ag (silver), Y (yttrium), Ti (titanium), Sn (tin), Li (lithium), germanium (germanium), etc. a rare earth element (it is also called a rare earth or RE), etc. may be contained. In order to make the cost price cheap, it is preferable to use above-mentioned Ag, Ti, Sn, Li and germanium, and the thing except a rare earth element etc.

[0020]

Mg alloy 10 comprises the Mg phase (henceforth alphaMg phase) 11 used as a host phase, an $Al_{12}Mg_{17}$ phase crystallized to the grain boundary of this alphaMg phase 11, and the granular CaMgSi phase 12 dispersed in the alphaMg phase 11. Other phases may be contained although alphaMg phase is contained especially in Mg phase.

This $Al_{12}Mg_{17}$ phase is an intermetallic compound of aluminum and magnesium, and while the hardness and strength of a Mg alloy can be raised, it reduces the stretch of a Mg alloy. $Al_{12}Mg_{17}$ phase is heat-treating Mg alloy 10, and is good to carry out solution

treatment of the $Al_{12}Mg_{17}$ phase, and to carry out prescription. Although this Mg alloy can also be made to crystallize the Al_2Ca phase and Mg_2Si phase which are mentioned below, when trying to perform the above-mentioned heat treatment, the effect of heat treatment is deteriorated according to crystallization of an Al_2Ca phase. For this reason, according to the purpose of using a Mg alloy, and the existence of heat treatment, crystallization of an Al_2Ca phase and Mg_2Si phase is controllable.

A CaMgSi phase is an intermetallic compound of calcium, magnesium, and silicon, and the hardness of a Mg alloy can be raised and it can also give heat resistance to a Mg alloy.

[0021]

Here, about the result of having considered the influence of temperature which the Mg alloy made crystallizing a CaMgSi phase has strongly, while referring to Fig.2, it describes. In the 0.3 mass % and Ca, the 1 mass % and Si are [the 0.7 mass % and Mn / the 1 mass % and the remainder] Mg and inevitable impurities, and, as for composition of the specimen of the used working example 1, Al makes Si of composition of the working example 1 which the 9 mass % and Zn described above the 2.00 mass %, as for composition of the specimen of the working example 2. On the other hand, although the specimen of a comparative example is AZ91 (for example, alloy equivalent to 2 type MC2 of the magnesium alloy castings of the description to JIS H 5203) which is a general-purpose alloy and there is an $Al_{12}Mg_{17}$ phase, there is no CaMgSi phase.

[0022]

In order to lose dispersion in the tensile strength by affectors, such as a defect, the smooth thing in which the artificial defect is not formed was used for the specimen of the comparative example at the specimen of the working examples 1 and 2 using the thing in which an artificial defect 2 mm in diameter and 2 mm in depth was formed.

Although there was some deterioration from the level which each tensile strength of the specimen (O) of the working example 1 and the specimen (**) of the working example 2 is regularity (125MPa) substantially to the temperature of 150 degrees C, and exceeded 150 degrees C as shown in Fig.2, there was no remarkable strength reduction. On the other hand, rapid strength reduction generated the specimen (**) of the comparative example with the rise of temperature.

in particular, in the strength of the specimen of the working examples 1 and 2, temperature became higher than the strength of the specimen of a comparative example in a region of 200 degrees C or more (here -- up to 250 degrees C).

[0023]

The above thing shows that the strength reduction under the hot environments of a Mg

alloy can be inhibited, and heat resistance can be made good by making a CaMgSi phase crystallize. The Mg alloy made to crystallize a CaMgSi phase is provided with sufficient fatigue strength, and Brinell-hardness H_B is about 110 and it is provided also with sufficient hardness.

Thus, since the influence by a CaMgSi phase is great to heat-resistant improvement in a Mg alloy, in order to make it crystallize a CaMgSi phase stably, let the amount of Ca in a Mg alloy be the 0.5 to 5 mass %, and let the amount of Si be the 0.5 - 5 mass %.

[0024]

Here, when the quantity of Ca and Si is less than the 0.5 mass %, the amount of CaMgSi(s) to crystallize decreases, a heat-resistant improved effect becomes small, and a fire-resistant effect decreases. On the other hand, when exceeding the 5 mass %, there is a possibility of the granular CaMgSi volume of phase to crystallize increasing too much, originating in this, and causing deterioration of fluidity.

For this reason, it is preferable to make a minimum into the 0.7 mass % and to make a maximum into the 3 mass %, although the amount of Ca in a Mg alloy was made into the 0.5 - 5 mass %, and although the amount of Si in a Mg alloy was made into the 0.5 - 5 mass %, it is preferable to make a minimum into the 0.7 mass % and to make a maximum into the 3 mass %.

[0025]

The grain boundary of alphaMg phase of a Mg alloy can be made to be able to crystallize an Al_2Ca phase further, and the hardness of a Mg alloy can also further be improved to it.

This Al_2Ca phase is an intermetallic compound of aluminum and calcium, and since it is hard and a high-melting point, it can also aim at further heat-resistant improvement in a Mg alloy.

Mg_2 Si phase (intermetallic compound of magnesium and silicon) can also be made to crystallize in alphaMg phase instead of the Al_2Ca phase crystallized to the grain boundary of alphaMg phase of a Mg alloy. Thereby, the creep resistance of a Mg alloy can be improved. This Mg_2 Si phase may be made to crystallize with an Al_2Ca phase.

[0026]

As shown above, since Mg alloy 10 makes the CaMgSi phase 12 crystallize in the alphaMg phase 11, it can be provided with sufficient heat resistance of the degree which can be used under an elevated-temperature situation (for example, 200 degrees C or more). Therefore, when this Mg alloy 10 is used for the engine material of an automobile, for example, a weight saving, friction, and reduction of printing can be aimed at, fuel consumption can be improved, and vibration and noise can also be reduced.

[0027]

Then, it describes about the manufacturing method of the Magnesium alloy concerning the 1 embodiment of the present invention.

First, a Mg-Al-Zn system alloy is prepared. alphaMg phase which this Mg-Al-Zn system alloy is AZ91 (specifically Mg -9 mass %Al-0.7 mass %Zn-0.3 mass %Mn) which is a general-purpose alloy, and turns into a host phase. It comprises an $Al_{12}Mg_{17}$ phase (intermetallic compound of aluminum and magnesium) crystallized to the grain boundary of this alphaMg phase.

The alloy which adds Ca and Si is not limited to this, as described above.

[0028]

Next, after heating the prepared Mg-Al-Zn system alloy more than the melting point and making it into a molten state, while adding and agitating Ca to this, it mixes. The amount of Ca in Mg alloy 10 obtained eventually adjusts this Ca addition amount so that it may become the within the scope of the 0.5 - 5 mass %.

And Si is added into the Mg-Al-Zn system alloy of a molten state in which Ca was added, and while heating and agitating the Mg-alloy raw material of this molten state in an 800-900 degrees C (they are preferably 860 degrees C and a maximum about a minimum 880 degrees C) temperature requirement, it mixes. The amount of Si in Mg alloy 10 obtained eventually adjusts this amount of added Si so that it may become the within the scope of the 0.5 - 5 mass %.

[0029]

When the heating temperature of the Mg-alloy raw material of the above-mentioned molten state is less than 800 degrees C, the temperature of a Mg-alloy raw material is largely less than the melting point (about 845 degrees C) of a CaMgSi phase, and the production efficiency of a CaMgSi phase is deteriorated. On the other hand, when exceeding 900 degrees C, heating temperature is too high, Mg oxidizes, and it causes deterioration of product quality.

By thus, the thing which the Mg-alloy raw material of the molten state added sequentially is heated, and Ca and Si cool and make solidify to ordinary temperature after that, Mg alloy 10 made to crystallize the alphaMg phase 11 used as a host phase, $Al_{12}Mg_{17}$ phase crystallized to the grain boundary of this alphaMg phase 11, and the granular CaMgSi phase 12 dispersed in the alphaMg phase 11 can be manufactured.

[0030]

After making a CaMgSi phase crystallize in the solidifying process of the Mg-alloy raw material in which Ca and Si were added, while heating this Mg-alloy raw material in a 600-800 degrees C temperature requirement, The grain boundary of alphaMg phase

may be made to crystallize an Al_2Ca phase by mixing, while added and agitating Ca except a CaMgSi phase in the Mg-alloy raw material of a molten state, and cooled and solidifying the Mg-alloy raw material in which Ca was added to ordinary temperature. The amount of Ca in the Mg alloy obtained eventually adjusts Ca addition amount here in consideration of Ca addition amount used for the above-mentioned formation of a CaMgSi phase so that it may become the within the scope of the 0.5 - 5 mass %.

Here, when temperature when adding Ca is less than 600 degrees C, a Mg alloy begins to solidify. On the other hand, when exceeding 800 degrees C, Ca which heating temperature is too high and is used for formation of an Al_2Ca phase is used for formation of a CaMgSi phase, and an Al_2Ca phase becomes is hard to be formed.

Therefore, it is preferable that the minimum of temperature when adding Ca shall be 650 degrees C, and a maximum shall be 750 degrees C.

[0031]

Mg_2 Si phase can also be made to crystallize in alphaMg phase instead of making the grain boundary of alphaMg phase crystallize an Al_2Ca phase. For example, after making a CaMgSi phase crystallize, while heating this Mg-alloy raw material, Mg_2 Si phase is made to crystallize in alphaMg phase by mixing, while added and agitating Si except a CaMgSi phase in the Mg-alloy raw material of a molten state, and cooled and solidifying the Mg-alloy raw material in which Si was added to ordinary temperature. Mg_2 Si phase may be made to crystallize with an Al_2Ca phase. The amount of Si in the Mg alloy obtained eventually adjusts the amount of added Si here in consideration of the amount of added Si used for the above-mentioned formation of a CaMgSi phase so that it may become the within the scope of the 0.5 - 5 mass %.

[0032]

By the above method, Mg alloy 10 provided with usable heat resistance under hot environments (200 degrees C or more) can be manufactured.

If it is in use of this Mg alloy 10, what is called a casting method that carries out a temperature rise and dissolve to the temperature from which organization constitution does not change, and cast in the mold for using the target form, and it makes it solidify can be used. However, without using the mold of the above-mentioned form, for example to what was cast to block like shape (form is not limited to this) etc., further, a forge, extrusion, or rolling can be processed and Mg alloy 10 can also be used. It may be machined.

Thereby, the obtained product can also be provided with usable heat resistance under hot environments.

[0033]

As mentioned above, although the present invention has been described with reference to an embodiment, the present invention is not limited to the composition of the description to the embodiment above-mentioned in any way, and also includes the other embodiments and modifications which are considered within the scope of the matter currently described in the scope of the claim. For example, it is contained in the scope of right of the present invention also when it constitutes a Magnesium alloy which has the heat resistance and fire retardancy of the present invention combining a part or all of each above-mentioned embodiment and modification, and a manufacturing method for the same.

In the aforementioned embodiment, it is usable in a Magnesium alloy in transport-airplane machines, such as other materials of an automobile, an airplane and a rail car, a machine part, a robot part article, etc.

[Explanations of letters or numerals]

[0034]

10: A Magnesium alloy, an 11:alphaMg phase, a 12:CaMgSi phase

DRAWINGS

[Drawing   1]

〈1〉

〈2〉

(54)HIGH STRENGTH MAGNESIUM ALLOY AND METHOD OF MANUFACTURING THE SAME

(57)Abstract

PROBLEM TO BE SOLVED: To provide a high strength magnesium alloy which shows high tensile strength, and is harder than the conventional material.

SOLUTION: The high strength magnesium alloy subjected to aging treatment includes, by mass: at least 16% and at most 34% of Zn; at least 0.3% and at most 2% of Si; at least 0.1% and at most 0.5% of Mn; and the remainder consisting of Mg, inevitable impurities, and a modifying element, based on 100 mass% of the whole magnesium alloy.

CLAIMS

[Claim(s)]

[Claim 1]

a time of being the Magnesium alloy which performed aging treatment and making the whole into the 100 mass % -- (-- only henceforth "%".)

16% or more and 34% or less of zinc (Zn),

0.3% or more and 2% or less of silicon (Si),

0.1% or more and 0.5% or less of manganese (Mn),

A high strength Magnesium alloy, wherein the remainder consists of magnesium (Mg), an inevitable impurity, and/or a refining element.

[Claim 2]

The high strength Magnesium alloy according to claim 1 which contains Zn 32% or less.

[Claim 3]

The high strength Magnesium alloy according to claim 1 or 2 which contains Zn 17% or more.

[Claim 4]

The high strength Magnesium alloy according to any one of claims 1 to 3 whose tensile strength is 180 or more MPa.

[Claim 5]

The high strength Magnesium alloy according to any one of claims 1 to 4 whose Vickers hardness numbers are 70 or more Hv(s).

[Claim 6]

a time of making the whole into the 100 mass % -- (-- only henceforth "%".)

16% or more and 34% or less of zinc (Zn),

0.3% or more and 2% or less of silicon (Si),

0.1% or more and 0.5% or less of manganese (Mn),

A manufacturing method of a high strength Magnesium alloy carrying out aging treatment of the Magnesium alloy, wherein the remainder consists of magnesium (Mg), an inevitable impurity, and/or a refining element.

[Claim 7]

A manufacturing method of the high strength Magnesium alloy according to claim 6 which performs the aforementioned aging treatment above 150 degrees C and below 300 degrees C.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

The present invention relates to the high strength Magnesium alloy whose strength improved by heat treatment.

[Background of the Invention]

[0002]

A Magnesium alloy still lighter-weight than an aluminum alloy is widely used as an aircraft material, a vehicles material, etc. in view of a weight saving. However, since the characteristic that a Magnesium alloy is required depending on a purpose is not exerted sufficiently, improvement in the further characteristic is called for.

[0003]

For example, although Magnesium alloys, such as AZ91D (ASTM sign), show high strength comparatively, wear has the defect that it is weak. The technique of dispersing the particles which change alloy composition and improve the hardness of the Magnesium alloy itself as a means which improves abrasion resistance, which stiffen a Magnesium alloy by heat treatment and which are rich in abrasion resistance, and making it combine with a Magnesium alloy etc. can be considered.

[0004]

For example, a Patent document 1 has disclosed the Magnesium alloy which contained zinc (Zn) 6.1% by weight, and contained 1.0 % by weight, silicon (Si), and 0.30 % by weight of manganese (Mn) and in which the remainder performed solution treatment and aging treatment to the alloy casting which consists of magnesium (Mg) as heat treatment (working example 13). This Magnesium alloy shows high tensile strength in ordinary temperature and 150 degrees C. The Magnesium alloy of the working example 3 which does not contain Zn 6.1% by weight and does not contain hidden Mn for Si 1.0% by weight shows tensile strength still higher than the working example 13. On the other hand, tensile strength in ordinary temperature of a Magnesium alloy of the comparative example 3 in which the remainder performed solution treatment and aging treatment to an alloy casting which consists of Mg including Zn and 1.0 % by weight of Si is 171MPa 20% by weight.

It is lower than tensile strength (224MPa) of the working example 13.

[Citation list]

[Patent literature]

[0005]

[Patent document 1] Japanese Published Patent Application No. H5-255794 (JP H5-255794A)

[Summary of Invention]

[Problem to be solved by the invention]

[0006]

Cited document 1 is estimating the tensile strength of the Magnesium alloy which performed aging treatment. However, it is not evaluated about the hardness of a Magnesium alloy. If Zn is included in an excess as it describes also in cited document 1, it will become weak, and it is described that tensile strength decreases. Therefore, the increase in the Zn content in a Magnesium alloy was hardly performed until now.

[0007]

The the object of this invention is as follows.

High tensile strength should be shown.

Provide a high strength Magnesium alloy harder than a conventional material.

[Means for solving problem]

[0008]

In the Mg-Zn-Si-Mn alloy, the inventor is adding many Zn contents rather than before, and acquired the new knowledge that a Magnesium alloy became hard. Although tensile strength was deteriorated with the increase in a Zn content in unmachined condition material, when the contained amount of Zn, Si, and Mn was a suitable range, it newly turned out by carrying out aging treatment that the strength of a Magnesium alloy is improved largely.

[0009]

namely, the time of the high strength Magnesium alloy of the present invention being a Magnesium alloy which performed aging treatment, and making the whole into the 100 mass % -- (-- only henceforth "%".)

16% or more and 34% or less of zinc (Zn),

0.3% or more and 2% or less of silicon (Si),

0.1% or more and 0.5% or less of manganese (Mn),

The remainder consists of magnesium (Mg), an inevitable impurity, and/or a refining element.

[0010]

The high strength Magnesium alloy of the present invention can also be regarded as a manufacturing method. namely, the time of the manufacturing method of the high

strength Magnesium alloy of the present invention making the whole the 100 mass % --
(-- only henceforth "%".)

16% or more and 34% or less of zinc (Zn),

0.3% or more and 2% or less of silicon (Si),

0.1% or more and 0.5% or less of manganese (Mn),

Aging treatment of the Magnesium alloy, wherein the remainder consists of magnesium
(Mg), an inevitable impurity, and/or a refining element is carried out.

[Effect of the Invention]

[0011]

The high strength Magnesium alloy of the present invention is harder than a
conventional material while it shows high tensile strength.

[Brief Description of the Drawings]

[0012]

[Drawing 1]It is a graph which shows the tensile strength to the Zn content of various
Magnesium alloys.

[Drawing 2]It is a graph which shows proof stress 0.2% to the Zn content of various
Magnesium alloys.

[Drawing 3]It is a graph which shows the hardness to the Zn content of various
Magnesium alloys.

[Drawing 4]It is the Photograph substituted for drawing in which the EPMA (electron
probe microanalyzer) reflection electron image (composition image) of
Mg-6.1Zn-0.3Si-0.5 Mn alloy is shown.

[Drawing 5]It is the Photograph substituted for drawing in which the EPMA reflection
electron image (composition image) of Mg-14Zn-0.4Si-0.2 Mn alloy is shown.

[Drawing 6]It is the Photograph substituted for drawing in which the EPMA reflection
electron image (composition image) of Mg-31Zn-0.4Si-0.2 Mn alloy is shown.

[Drawing 7]It is the Photograph substituted for drawing in which the EPMA reflection
electron image (composition image) of Mg-51Zn-0.4Si-0.2 Mn alloy is shown.

[Drawing 8]It is the Photograph substituted for drawing in which the EPMA reflection
electron image (composition image) of Mg-17Zn-1.4Si-0.2 Mn alloy is shown.

[Drawing 9]It is the Photograph substituted for drawing in which the EPMA reflection
electron image (composition image) of Mg-21Zn-1.5Si-0.2 Mn alloy is shown.

[Drawing 10]It is the Photograph substituted for drawing in which the EPMA reflection
electron image (composition image) of Mg-35Zn-2.0Si-0.2 Mn alloy is shown.

[Description of Embodiments]

[0013]

The embodiment of invention is mentioned and the present invention is described in more detail.

[0014]

The present invention is characterized by a high strength Magnesium alloy comprising the following.

It is the Magnesium alloy which performed aging treatment, and is Zn.

Si.

Mn.

The remainders are Mg, an inevitable impurity, and/or a refining element.

[0015]

Zn is an element which dissolves to alpha-magnesium crystal grain (alpha phase), and improves the mechanical strength of a Magnesium alloy. In the Magnesium alloy of the present invention with more Zn contents than usual, Zn system crystallized material like $MgZn_2$ crystallizes to three-dimensional mesh shape in the grain boundary of an alpha-Mg crystal grain. Therefore, a Magnesium alloy becomes hard, so that there are many Zn contents. However, the tensile strength of the Magnesium alloy before heat treatment tends to be deteriorated, so that there is much contained amount of Zn. If a Zn content is 16% or more, the strength of a Magnesium alloy will be largely improved by carrying out aging treatment. A preferable Zn content is 20% or more still more preferably 18% or more 17% or more, and tensile strength and proof stress comparable as a Magnesium alloy with low hardness with few Zn contents are acquired. However, big and rough $MgZn_2$ crystallizes to the grain boundary that Zn is excessive, the network structure is divided, and ductility is deteriorated largely. Therefore, a Zn content is made into 34% or less. Preferably, it is 30% or less still more preferably 31% or less 32% or less.

[0016]

In a Magnesium alloy with few Zn contents, Si is crystallized as Mg_2Si to the grain boundary of an alpha-Mg crystal grain, and improves a mechanical strength. In the Magnesium alloy of the present invention, since a lot of Zn exists with Si, Si contributes to improvement in tensile strength and hardness with Zn system crystallized material. A Si content is made into 0.3% or more. However, Mg_2Si crystallizes that Si is excessive as a big and rough primary phase, and it makes a mechanical strength be deteriorated. Liquid phase temperature rises with the increase in the amount of Si, and the fluidity in the case of casting worsens. Therefore, a Si content is made into 2% or less. Preferably, it is 1.6% or less still more preferably 1.8% or less.

[0017]

Mn is an element which dissolves to alpha phase like Zn and improves the mechanical strength of a Magnesium alloy. It is surmised that the improved effect of the strength by aging treatment enlarges the Magnesium alloy of the present invention with more Zn contents than before by existence of Mn. However, a big and rough massive compound crystallizes to a grain boundary that Mn is excessive, and ductility is deteriorated. Therefore, desirable Mn contents are 0.1% or more and 0.5% or less.

[0018]

As an inevitable impurity contained in the Magnesium alloy of the present invention, Al, Fe, nickel, Cu, Cl, Ca, K, Be, etc. are mentioned, for example. As for each of these inevitable impurities, it is preferable to consider it as 0.01 more% or less 0.02% or less.

[0019]

The Magnesium alloy of the present invention may add the refining element for improving the various characteristics, such as a metal texture, oxidation resistance, corrosion resistance, and an electrical property. That is, addition of a publicly known refining element is not barred to the Magnesium alloy of the present invention. As a refining element, Sr, Y, Zr, etc. are mentioned, for example. The contained amount of each of these elements is adjusted with the characteristic required of a Magnesium alloy as appropriate. The viewpoints of cost, the influence on basic composition, etc. to a refining element has a preferable 0.8% or less 0.6 more% or less degree 1% or less in a content total amount.

[0020]

The Magnesium alloy of the present invention is high strength, and hard. If it specifies specifically, the tensile strength of the Magnesium alloy of the present invention is good in their being 180 or more MPa and 200 more MPa or more of 190 or more MPa. The hardness of the Magnesium alloy of the present invention is good in it being 70 or more, 75 or more, 80 or more, and further 100 or more [85 or more] in Vickers hardness number. It is good for measurement of tensile strength to do a regular tensile test on JIS.

[0021]

As long as a Magnesium alloy has the composition mentioned above, ingot material or a sintering material may be sufficient as it. In order to prevent oxidation of the Magnesium alloy under an ingot or sintering, it may be cast or sintered by antioxidant atmosphere and also a vacuum atmosphere. When casting a Magnesium alloy, it is good for there to be no limitation in particular in the cooling rate, for example, to cool slowly in the atmosphere. It may cast using any of a sand mold and a mold.

[0022]

Heat treatment performed to a Magnesium alloy is aging treatment. With the Magnesium alloy of the present invention with comparatively many Zn contents, it is surmised including Zn, Si, and Mn that a minute sludge is generated effectively and tensile strength improves by performing aging treatment at least. It is preferable to perform aging treatment above 180 more degrees C above 150 degrees C and below 300 degrees C and below 250 degrees C to a Magnesium alloy with the composition included in the above-mentioned range acquired by casting etc. Although there is no limitation that the processing time should just select suitable time, 30 minutes or more and 8 hours or less are suitable. Although only aging treatment may perform (what is called T5 processing), heat treatment may perform aging treatment (what is called T6 processing), after performing solution treatment before aging treatment. As for solution treatment, it is preferable to carry out above 300 degrees C and below 400 degrees C in general.

[0023]

The Magnesium alloy of the present invention is high strength, and since it is hard, it is excellent in abrasion resistance. Therefore, it is suitable to be used for the cylinder block for automobile engines, a bedplate, an oil pan mechanism, the housing for compressors, a cylinder, etc.

[0024]

As mentioned above, although the embodiment of the present invention was described, the present invention is not limited to the above-mentioned embodiment. In the range which does not deviate from the summary of the present invention, it can carry out with various forms which performed change which a person skilled in the art can make, improvement, etc.

[Working example]

[0025]

An working example is given and the present invention is described more specifically.

[0026]

Multiple specimens which changed the contained amount of the alloy element in a Magnesium alloy were manufactured, and evaluation of those characteristics and observation of the metal texture were performed.

[0027]

[Production of specimen #01-#05 and #11 - #21]

The flux of a chloride system was applied to the inner surface of the iron crucibles preheated in the electric furnace, pure Zn was supplied [the pure magnesium metal, pure Si, pure Mn, and if needed] which were weighed in it, and it dissolved at 750

degrees C. After stirring this molten metal sufficiently and dissolving a raw material completely, stillness holding was carried out for a while at 700 degrees C. Slushed into the iron molds of predetermined form various kinds of molten metals obtained in this way, and carry out air cooling, it was made to solidify in the atmosphere, and each specimen (magnesium alloy castings) was cast. The obtained specimen was 20mmx30mmx200mm.

[0028]

The chemical composition of each specimen was shown in Table 1. "Analysis composition" of Table 1 was measured by the ultimate analysis by fluorescence-X-rays (XRF) analysis. The same specimen (#00) was produced from commercial AZ91D.

[0029]

Aging treatment for 1 to 8 hours (T5 processing) was performed to each specimen shown in Table 1 at 200 degrees C among the atmosphere. A tensile test and Vickers hardness number measurement were performed in the following procedures to each specimen (heat treatment material) after aging treatment. In addition to a tensile test and Vickers hardness number measurement, measurement of thermal conductivity and a stress relaxation examination were done about the unmachined condition material before heat treatment as a reference example.

[0030]

[Tensile test]

From each of each specimen (unmachined condition material and heat treatment material) shown in Table 1, the No. 14 test piece for tensile test of JISZ2201 was produced, the tensile test of JISZ2241 was done in the room temperature, and it asked for tensile strength, a stretch, 0.2% proof stress, and Young's modulus. The result was shown in Table 1. The tensile strength to a Zn content was shown in Fig.1, and proof stress was shown in Fig.2 0.2%, respectively.

[0031]

[Vickers hardness number measurement]

About each specimen (unmachined condition material and heat treatment material) shown in Table 1, Vickers hardness number measurement was performed in the room temperature. Vickers hardness number measurement was performed by measuring-load 10kgf to the section of a specimen central part using the Vickers hardness tester. The measurement result was shown in Table 1 and Fig.3.

[0032]

[Measurement of thermal conductivity]

About each specimen (unmachined condition material) produced in the

above-mentioned procedure, it asked for thermal conductivity with laser flash method. The test result was shown in Table 1.

[0033]

[Stress relaxation examination]

About each specimen (unmachined condition material) shown in Table 1, the stress relaxation examination was done and the creep resistance of the Magnesium alloy was investigated. The stress relaxation examination measured the process in which stress when load is added to a specimen to predetermined deformation among test time decreased with time. It combined with the lapse of time and made the compression stress be deteriorated so that the compression stress of 100MPa may be loaded on a specimen and displacement of the specimen at that time may be specifically kept constant into 150 degrees C atmospheric air. The value of the compression stress 40 hours after the start of test was shown in Table 1 as a ratio (stress retention) over an early value.

[0034]

[Table 1]

No	配合組成（質量%）			分析組成（質量%）			測定結果（鋳放し材）							測定結果（熱処理材）				
							熱伝導率	応力保持率	引張試験				硬さ	引張試験				硬さ
	Si	Zn	Mn	Si	Zn	Mn			ヤング率	引張強さ	伸び	0.2%耐力		ヤング率	引張強さ	伸び	0.2%耐力	
							W/mK	%	MPa	MPa	%	MPa	Hv	MPa	MPa	%	MPa	Hv
#01	0.5	6.0	0.5	0.3	6.1	0.5	124	73	54	160	4.5	77	56	42	210	6.0	120	61
#02	0.5	15	0.3	0.4	14	0.2	85	74	46	120	0.7	94	74	43	153	0.7	138	85
#03	0.5	30	0.3	0.4	31	0.2	62	77	52	83	0.2	–	122	52	210	0.6	197	147
#04	0.5	50	0.3	0.4	51	0.2	26	93	–	0	0.0	–	217	–	0	0.0	–	229
#05	1.0	15	0.3	0.7	13	0.2	93	73	51	133	0.9	103	73	51	229	1.8	172	85
#11	1.5	0.0	0.5	0.9	0.0	0.2	165	56	34	148	5.6	61	44	–	–	–	–	–
#12	1.5	1.0	0.5	1.1	1.4	0.3	139	53	40	165	6.1	64	51	38	142	3.4	66	52
#13	1.5	2.0	0.5	1.1	2.2	0.3	117	61	38	165	5.5	64	50	39	150	4.2	66	55
#14	1.5	3.0	0.5	1.3	3.1	0.2	126	63	42	176	7.9	59	55	40	171	5.9	71	58
#15	1.5	4.5	0.5	1.2	4.6	0.2	133	64	45	170	4.6	77	54	39	171	4.2	86	63
#16	1.5	6.0	0.5	0.9	6.0	0.3	117	75	45	144	3.2	68	56	44	218	6.8	104	66
#17	1.5	9.0	0.5	1.4	8.5	0.2	109	79	43	152	2.5	84	65	45	191	2.0	127	72
#18	1.5	12	0.5	1.3	8.9	0.3	98	78	46	153	1.2	106	75	47	180	1.0	150	78
#19	1.5	20	0.5	1.4	17	0.2	77	78	44	157	0.7	143	98	45	236	1.1	201	108
#20	1.5	25	0.5	1.5	21	0.2	68	78	46	131	0.3	–	114	48	197	0.6	–	125
#21	1.5	40	0.5	2.0	35	0.2	39	89	–	13	0.0	–	183	47	57	0.1	–	203
#22	2.0	6.0	0.5	1.6	6.1	0.2	116	73	43	156	2.8	90	63	41	176	2.6	115	65
#00	AZ91D						58	70	40	189	4.7	85	63	–	–	–	–	–

ECOMETAL-002164

The tensile strength of AZ91D shown in the graph of Fig.1 - Fig.3 is a reference value for comparison, and is not a value depending on the amount of Zn.

[0035]

[Observation of a metal texture]

The metal texture of #01-#04 before heat treatment and #19 after heat treatment - #21 was observed among the specimens shown in Table 1. The reflection electron image (composition image) of EPMA (electron probe microanalyzer) was acquired from the section cut out from each specimen. The audit observation was shown in Fig.4 - Fig.10. Surface analysis of the same surface was conducted by EPMA (not shown). When the texture observation result and the result of the surface analysis by EPMA were the same specimens, it is before and after heat treatment, and checked that a big difference did not arise.

[0036]

[About the measurement result of unmachined condition material]

Vickers hardness number suited the improving tendency as the Zn content increased (Fig.3). In the range whose Zn content is 0 to 4%, it went up as the Zn content increased, but at 4 to 10%, tensile strength was deteriorated with the increase in a Zn content, and when 10% was exceeded, it was further deteriorated (Fig.1). About 0.2% proof stress, the direction with many Zn contents suited the tendency which shows a high value (Fig.2).

[0037]

When the Zn content was 30% or less, it turned out equivalent to AZ91D, or that it has the thermal conductivity and creep resistance beyond it. Therefore, the same characteristic as unmachined condition material is expected also about heat treatment material.

[0038]

Fig.4 and Fig.5 show the EPMA reflection electron image (composition image) of #01 with insufficient Vickers hardness number, and #02, respectively. Analysis by EPMA showed that $MgZn_2$ and Mg_2Si had crystallized to the grain boundary of an alpha-Mg crystal grain. However, as for it, such crystallized material turned out that not mesh shape but it is divided and exists in the grain boundary. On the other hand, in #19, #20, and #03, the crystallized material generated by three-dimensional mesh shape in the grain boundary of the alpha-Mg crystal grain was observed (Fig.6, Fig.8, and Fig.9). As for the compound crystallized to the grain boundary, analysis by EPMA showed that

most was $MgZn_2$. In #21 with still more Zn contents, the ratio that the grain boundary crystallized material in an alloy occupies increased. In #04 whose a Zn content is 50%, $MgZn_2$ big and rough to the grain boundary was seen (Fig.7).

[0039]

[About the measurement result of heat treatment material]

Vickers hardness number of any specimen improved by heat treatment. After heat treatment, Vickers hardness number suited the improving tendency as the Zn content increased (Fig.3). The Vickers hardness numbers of the specimen which contains Zn 16% or more were 100 or more Hv(s). Although #21 and #04 whose a Zn content is 35% or more were very hard, the stretch was almost a weak material of 0.

[0040]

It turned out that tensile strength of tensile strength will improve by aging treatment from Fig.1 if a Zn content is 5% or more. With the specimen after heat treatment, the improvement in about 50% or more of tensile strength (being before and after heat treatment difference of about 65 or more MPa) was considered for a Zn content to be 16% or more to the tensile strength of the specimen before heat treatment. However, when the Zn content exceeded 34%, deterioration of the tensile strength accompanying the increase in a Zn content appeared notably.

[0041]

It was the tendency same also about 0.2% proof stress as tensile strength. Especially as for #13 whose tensile strength improved largely by heat treatment, the 0.2% proof stress after heat treatment was deteriorated. The value was equivalent to AZ91D of an unmachined condition. That is, in order to have satisfied mechanical property sufficient after heat treatment, it turned out that it is good to make a Zn content into further 17 to 31% 16 to 34%. Especially the preferable Si content in this case was 0.4 to 1.5%. As for a Zn content, when ductility is taken into consideration, it is preferable that it is [16 to 20%] further 16 to 18%.
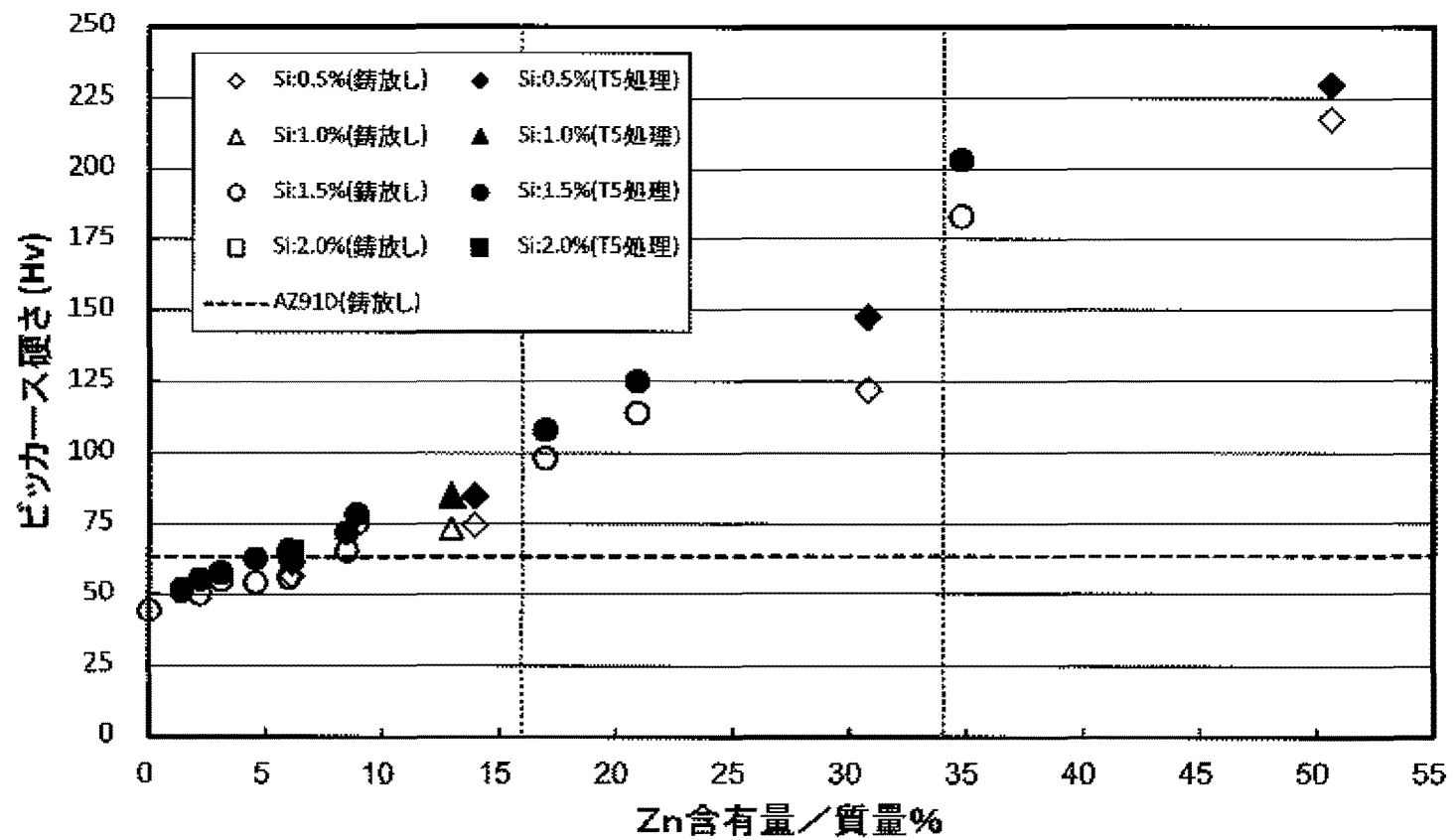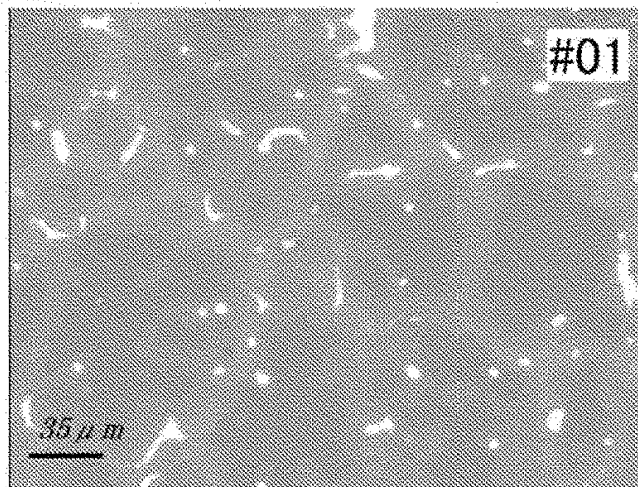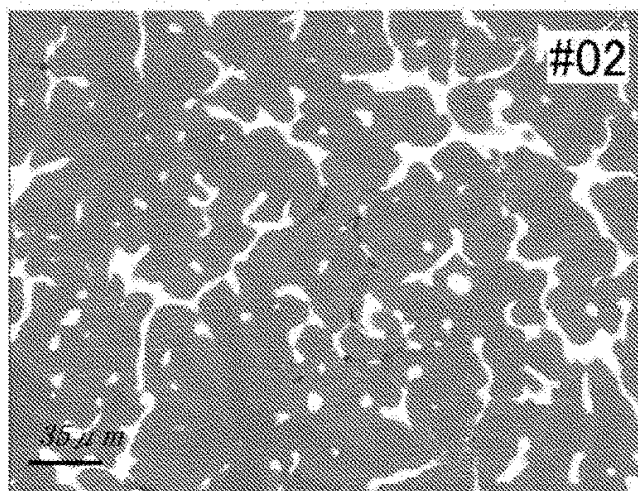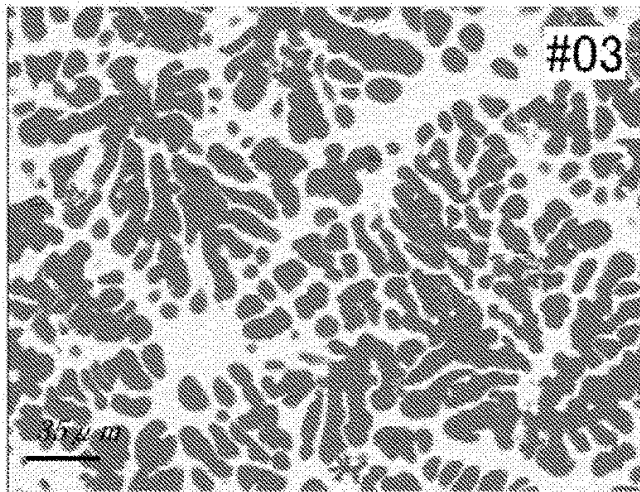
DRAWINGS

[Drawing 1]

[Drawing 2]

縦軸: 0.2%耐力／MPa
横軸: Zn含有量／質量%

凡例:
◇ Si:0.5%(鋳放し)　　◆ Si:0.5%(T5処理)
△ Si:1.0%(鋳放し)　　▲ Si:1.0%(T5処理)
○ Si:1.5%(鋳放し)　　● Si:1.5%(T5処理)
□ Si:2.0%(鋳放し)　　■ Si:2.0%(T5処理)
- - - AZ91D(鋳放し)

[Drawing 3]

[Drawing 4]

#01

35 μm

[Drawing 5]

#02

35 μm

[Drawing 6]

[Drawing 7]

#04

[Drawing 8]

#19

[Drawing 9]

[Drawing 10]

(54)MAGNESIUM ALLOY FOR CASTING, AND MAGNESIUM ALLOY CASTING

(57)Abstract

PROBLEM TO BE SOLVED: To provide a magnesium alloy for casting suitable for use at high temperature.

SOLUTION: The magnesium alloy for casting includes, by mass, 1 to 5% copper (Cu), 0.1 to 5% calcium (Ca) and 0.1 to 5% silver (Ag), and the balance magnesium (Mg) with inevitable impurities. By the incorporation of Cu and Ca, the crystallized products of an Mg-Cu based compound and an Mg-Ca based compound are crystallized out on the crystal grain boundaries of Mg crystal grains, so as to be a three-dimensional network shape. By the three-dimensional network structure, boundary sliding particularly activated when temperature is made high is suppressed, so as to improve its high temperature strength and high temperature creep strength. Further, by the addition of Ag, the Mg crystal grains are made fine, and the three-dimensional network structure having high continuity and dense can be formed. Also, Ag hardly exerts adverse influence on the thermal conductivity of the magnesium alloy.

CLAIMS

[Claim(s)]

[Claim 1]

A Magnesium alloy for casting characterized by comprising the following.

When the whole is made into the 100 mass %, it is copper (Cu) more than the 1 mass % and below the 5 mass %.

Calcium more than the 0.1 mass % and below the 5 mass % (Ca).

Silver (Ag) more than the 0.1 mass % and below the 5 mass %.

An implication and the remainder are magnesium (Mg) and an inevitable impurity.

[Claim 2]

The Magnesium alloy for casting according to claim 1 whose aforementioned copper (Cu) is more than the 2 mass % and below the 4 mass %.

[Claim 3]

The Magnesium alloy for casting according to claim 1 whose aforementioned calcium (Ca) is more than the 0.5 mass % and below the 3 mass %.

[Claim 4]

The Magnesium alloy for casting according to claim 1 whose aforementioned silver (Ag) is more than the 0.1 mass % and below the 3 mass %.

[Claim 5]

When the whole is made into the 100 mass %, copper (Cu) more than the 1 mass % and below the 5 mass %, A teeming process of carrying out teeming of the molten metal which the remainder becomes from magnesium (Mg) and an inevitable impurity to a mold including calcium (Ca) more than the 0.1 mass % and below the 5 mass %, and silver (Ag) more than the 0.1 mass % and below the 5 mass %,

A coagulating process which is made to cool a molten metal after the teeming process, and is solidified,

************** -- magnesium alloy castings characterized by things.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

The present invention relates to the Magnesium alloy for casting suitable for the use under an elevated temperature.

[Background of the Invention]

[0002]

A Magnesium alloy still lighter-weight than an aluminum alloy is widely used as an aircraft material, a vehicles material, etc. in view of a weight saving. However, depending on the purpose, since neither strength nor heat resistance is sufficient, the Magnesium alloy is asked for improvement in the further characteristic.

[0003]

For example, there is AZ91D (ASTM sign) as a common Magnesium alloy. Since it is 73 W/mK degree, when an operating environment is used for the component which is an elevated temperature or generates heat while in use, heat dissipation is not performed satisfactorily but heat deformation may produce the thermal conductivity of AZ91D in a component. If a Magnesium alloy with low thermal conductivity is used as a Magnesium alloy especially used for the cylinder head and cylinder block of an internal-combustion engine, The adverse effect of a cylinder head carrying out heat deformation, or friction increasing because it is filled with heat and a cylinder bore deforms into a cylinder block, or airtightness being deteriorated arises. Therefore, heat dissipation is satisfactorily performed by having high thermal conductivity, and the use under an elevated temperature is asked for the suitable Magnesium alloy.

[0004]

For example, the thermal conductivity of a Magnesium alloy with the alloy composition (a unit is "the mass %") of Mg-3%Cu-1%Ca is that Cu with high thermal conductivity is contained, and is higher than the thermal conductivity of AZ91D. However, depending on a service condition, the creep resistance in an elevated temperature, etc. may not be sufficient.

[0005]

A Patent document 1 has disclosed the Magnesium alloy containing calcium (Ca) of the 0.8 - 5 mass %, copper (Cu) of the 0 - 10 mass %, and the zinc (Zn) of the 3 - 8 mass %. Although the Magnesium alloy of a Patent document 1 shows high strength in a room temperature and an elevated temperature, it is unknown whether there is no description about thermal conductivity and zincky addition influences the thermal

conductivity of a Magnesium alloy.

[Patent document 1] Japanese Published Patent Application No. H6-25791 (JP H6-25791A)

[Description of the Invention]

[Problem to be solved by the invention]

[0006]

An object of the present invention is to provide the Magnesium alloy for casting suitable for the use under an elevated temperature in view of the above-mentioned problem. It aims at providing the casting which consists of the Magnesium alloy for casting.

[Means for solving problem]

[0007]

The inventors are adding silver with copper and calcium as an alloy element of a Magnesium alloy intensively as a result of research. It finds out that hot creep resistance can be improved without having an adverse effect on the thermal conductivity of a Magnesium alloy, and came to complete the present invention based on this.

[0008]

That is, a Magnesium alloy for casting of the present invention comprises the following: When the whole is made into the 100 mass %, it is copper (Cu) more than the 1 mass % and below the 5 mass %.

Calcium more than the 0.1 mass % and below the 5 mass % (Ca).

Silver (Ag) more than the 0.1 mass % and below the 5 mass %.

An implication and the remainder are magnesium (Mg) and an inevitable impurity.

[0009]

The magnesium alloy castings of the present invention are castings which consists of the Magnesium alloy for casting of the present invention. Magnesium alloy castings of the present invention,

When the whole is made into the 100 mass %, copper (Cu) more than the 1 mass % and below the 5 mass %, The teeming process of carrying out teeming of the molten metal which the remainder becomes from magnesium (Mg) and an inevitable impurity to a mold including calcium (Ca) more than the 0.1 mass % and below the 5 mass %, and the silver (Ag) more than the 0.1 mass % and below the 5 mass %,

The coagulating process which is made to cool the molten metal after the teeming process, and is solidified,

*************** -- it is characterized by things.

[Effect of the Invention]

[0010]

The crystallized material of a Mg-Ca system compound crystallizes the Magnesium alloy for casting of the present invention in the shape of a network (three-dimensional mesh shape) to the grain boundary of Mg crystal grain with a Mg-Cu system compound by including Cu and Ca. The grain boundary slide which will become active especially according to a three-dimensional network if it becomes an elevated temperature is inhibited, and high temperature strength and the creep resistance in an elevated temperature improve.

[0011]

The Magnesium alloy for casting of the present invention is that Ag is included with Cu and Ca, Mg crystal grain becomes minute and a three-dimensional network with it is formed. [high continuity and] [precise] Unlike other alloying elements, such as aluminum, Ag has few adverse effects to the thermal conductivity of a Magnesium alloy.

[0012]

In this Description, the description of a "X-Y system compound" etc. is a compound which carries out the main component of X as indicated to be X_2Y with an empirical formula, and the Y, for example.

[Best Mode of Carrying Out the Invention]

[0013]

The best form for below carrying out the Magnesium alloy for casting of the present invention is described.

[0014]

As for the Magnesium alloy for casting of the present invention, the remainder consists of magnesium (Mg) and an inevitable impurity including copper (Cu), calcium (Ca), and silver (Ag).

[0015]

The Magnesium alloy for casting of the present invention is making contained amount of Cu, Ca, and Ag into a suitable quantity, and the crystallized material of a Mg-Cu system compound and a Mg-Ca system compound crystallizes it in the shape of a network (three-dimensional mesh shape) to the grain boundary of Mg crystal grain. Since a three-dimensional network with few discontinuous parts is formed in the grain boundary, the depressor effect of a grain boundary slide is high.

[0016]

The contained amount of Cu is more than the 1 mass % and below the 5 mass %, when the whole Magnesium alloy for casting is made into the 100 mass %. If the contained

amount of Cu is more than the 1 mass %, a Mg-Cu system compound will crystallize sufficiently to the grain boundary. With less than the 1 mass %, since crystallization to the grain boundary of a Mg-Cu system compound is insufficient, the contained amount of Cu has low strength. The preferable contained amount of Cu is more than the 2 mass %. On the other hand, since the quantity of the Mg-Cu system compound crystallized to the grain boundary serves as an excessive next door and a weak organization, strength is deteriorated, so that there is much Cu. The preferable contained amount of Cu is below the 4 mass %.

[0017]

The Magnesium alloy for casting of the present invention contains Ca and Ag with Cu. Ca and Ag exist in the grain boundary with Cu, and are considered to contribute to formation of a three-dimensional network. Specifically, a Mg-Ca system compound crystallizes to the grain boundary with a Mg-Cu system compound, and it is surmised that a precise three-dimensional network is formed by the addition effect of Ag.

[0018]

The contained amount of Ca is more than the 0.1 mass % and below the 5 mass %, when the whole Magnesium alloy for casting is made into the 100 mass %. If the contained amount of Ca is more than the 0.1 mass %, a Mg-Ca system compound will crystallize sufficiently to the grain boundary. Since the ignition temperature of a Magnesium alloy will rise if Ca is added to a Magnesium alloy, the combustion which may occur when a Magnesium alloy is made into a molten metal is prevented. The contained amount of preferable Ca is more than the 0.5 mass %. On the other hand, when the content ratio of Ca exceeds the 5 mass %, the generated amount of grain boundary crystallized material may increase too much, mechanical properties, such as tensile strength and a stretch, may be deteriorated, and it may produce a problem in post processing. The contained amount of preferable Ca is below a 3 mass % less or equal and also the 2 mass %.

[0019]

The contained amount of Ag is more than the 0.1 mass % and below the 5 mass %, when the whole Magnesium alloy for casting is made into the 100 mass %. Since the solid-liquid coexisting temperature range will become narrow and will become minute [Mg crystal grain] if the contained amount of Ag is more than the 0.1 mass %, a precise three-dimensional network is formed. Although the width of grain boundary crystallized material becomes thick and high temperature strength and the creep resistance in an elevated temperature improve, there is a tendency for the mobility of a molten metal to be deteriorated, cost also becomes high, and the particle diameter of Mg crystal grain is not so economical as there are many content ratios of Ag as the content ratio of Ag

increases, while it becomes small. Therefore, as for the contained amount of Ag, below the 5 mass % carries out. The contained amount of preferable Ag is below a 4 mass % less or equal and also the 3 mass %.

[0020]

The Magnesium alloy for casting of the present invention described above can make the field of the universe and aeronautical navigation the start, and it can be used for it in various fields, such as an automobile and an electrical machinery and apparatus. As a component which consists of the Magnesium alloy for casting of the present invention, The product used under hot environments taking advantage of the characteristic in an elevated temperature. For example, the parts which constitute the compressor, the pumps, and the various cases used as an elevated temperature while in use, The engine part used under an elevated temperature and a heavy load, the transmission case especially used for the cylinder head of an internal-combustion engine, a cylinder block, an oil pan mechanism, the impeller for turbochargers of an internal-combustion engine, an automobile, etc., etc. are mentioned.

[0021]

The magnesium alloy castings of the present invention are castings which consists of the Magnesium alloy for casting of the present invention explained in full detail above. Namely, the magnesium alloy castings of the present invention are a teeming process and a coagulating process castings pass, and a teeming process, When the whole is made into the 100 mass %, copper (Cu) more than the 1 mass % and below the 5 mass %, Calcium (Ca) more than the 0.1 mass % and below the 5 mass %, and the silver (Ag) more than the 0.1 mass % and below the 5 mass %, the process which makes it cool and the process and coagulating process which carry out teeming of the molten metal which an implication and the remainder become from magnesium (Mg) and an inevitable impurity to a mold make solidify the molten metal after a teeming process -- it comes out.

[0022]

What carried out die casting not only in usual gravity casting and application-of-pressure casting may be sufficient as the magnesium alloy castings of the present invention. The mold used for casting does not ask a sand mold, a mold, etc., either. There may be no limitation in particular also in the coagulation speed (cooling rate) in a coagulating process, and it may choose the coagulation speed which is a degree in which a three-dimensional network is formed as appropriate according to the size of an ingot. If it is made to solidify at a general coagulation speed, a network-like metal texture will be obtained.

[0023]

As for the Magnesium alloy for casting and magnesium alloy castings of the present invention, it is desirable that it is unmachined condition material. The cast characteristic may be improved by heat-treating after casting.

[0024]

As mentioned above, although the embodiment of the Magnesium alloy for casting of the present invention and magnesium alloy castings was described, the present invention is not limited to the above-mentioned embodiment. In the range which does not deviate from the summary of the present invention, it can carry out with various forms which performed change which a person skilled in the art can make, improvement, etc.

[Working example]

[0025]

An working example is given to below and the present invention is described specifically.

[0026]

Multiple specimens which changed the contained amount of the alloy element in a Magnesium alloy were manufactured, and evaluation of those characteristics and observation of the metal texture were performed.

[0027]

[Production of specimen #01 - #05]

The flux of a chloride system was applied to the inner surface of the iron crucibles preheated in the electric furnace, and [the pure magnesium metal, pure Cu, and if needed] which were weighed in it, pure Ag was supplied and it dissolved. Ca weighed in this molten metal held at 750 degrees C was added (molten metal preparation process).

[0028]

After stirring this molten metal sufficiently and dissolving a raw material completely, stillness holding was carried out for a while at the temperature. Slushed into the mold of predetermined form various kinds of molten metals obtained in this way (teeming process), it was made to solidify in atmospheric air (coagulating process), and the specimen (magnesium alloy castings) of #01 - #05 was cast. The obtained specimen was 30mmx30mmx200mm. The chemical composition of each specimen is shown in Table 1.

[0029]

[Measurement of thermal conductivity]

In addition to the specimen of #01 produced in the above-mentioned procedure - #05, it asked for thermal conductivity with the laser flash method about the same specimen produced from commercial AZ91D (composition is described in Table 1). A test result is

shown in Table 1 and Fig.1.

[0030]

[Stress relaxation examination]

About the specimen produced from specimen #01-#05 and AZ91D which were shown in Table 1, the stress relaxation examination was done and the creep resistance of the Magnesium alloy was investigated. A stress relaxation examination measures the process in which stress when load is added to a specimen to predetermined deformation among test time decreases with time. It combined with the lapse of time and made the compression stress be deteriorated so that the compression stress of 100MPa may be loaded on a specimen and displacement of the specimen at that time may be specifically kept constant into 200 degrees C atmospheric air. The stress decrease amount 40 hours after the start of test is shown in Table 1 and Fig.2. The graph which plotted and created the compression stress added to a specimen every 10 minutes is shown in Fig.3.

[0031]

[Observation of a metal texture]

The surface of specimen #01 shown in Table 1 - #05 was observed. Surface observation observed the section cut out from each specimen with the metallurgical microscope, and it performed it. # Although the metal texture of the surface of 01 - #05 was shown in Fig.4 - Fig.8, respectively, in each figure, (a) observed low magnification and (b) observed the same section with high magnification.

[0032]

In specimen #01, the three-dimensional network which an intermetallic compound crystallizes to the grain boundary was checked so that Fig.4 (a) might show. In Fig.4 (b), it is $CuMg_2$ that looks brightly in the grain boundary, and it checked that it was Mg_2Ca that looks darkly by EPMA (electron probe microanalyzer) and XRD (X-ray diffraction). In specimen #02-#05, the three-dimensional network with high continuity whose meshes of a net are finer than #01 was checked so that Fig.5 (a) - Fig.8 (a) might show. In Fig.5 (b) - Fig.8 (b), it is $CuMg_2$ that looks brightly in the grain boundary, and it checked that it was Mg_2Ca that looks darkly by EPMA and XRD.

[0033]

According to EPMA and XRD, in specimen #02 - #05, Ag has checked mainly existing as Ag_3Mg in the grain boundary.

[0034]

[Table 1]

No.	合金組成[質量%]	熱伝導率 [W/mK]	応力低下量 [MPa]
#01	Mg-3%Cu-1%Ca	155	65
#02	Mg-3%Cu-1%Ca-0.1%Ag	162	63
#03	Mg-3%Cu-1%Ca-1%Ag	154	59
#04	Mg-3%Cu-1%Ca-2%Ag	160	58
#05	Mg-3%Cu-1%Ca-3%Ag	156	56
AZ91D	Mg-9%Al-1%Zn	73	60

[0035]

Each of specimens of 01 - #05 excelled AZ91D in thermal conductivity. Although the thermal conductivity of the specimen of #01 which does not contain Ag was 155 W/mK, in the specimen of #02 - #05, the thermally conductive deterioration by addition of Ag was not seen.

[0036]

There were so few stress decrease amounts 40 hours after the start of test in a stress relaxation examination at 200 degrees C that there was much contained amount of Ag. It went especially over each specimen of #03, #04, and #05 by 40 hours from the start of test, and the creep resistance superior to the specimen of #01 which does not contain Ag, or AZ91D was shown (Fig.3).

[0037]

Each of above-mentioned specimens made Cu the 3 mass %, and set Ca constant with the 1 mass %. Also in which specimen, if it is Cu, if it is Ca, above-mentioned thermal conductivity and creep resistance comparable as each specimen are shown in the range more than the 0.7 mass % and below the 1.3 mass % as for more than the 2.7 mass % and below the 3.3 mass %.

[0038]

That is, the thermally conductive deterioration by addition of Ag is not seen, but the Magnesium alloy containing Cu, Ca, and Ag of suitable contained amount is excellent in hot creep resistance.

[Brief Description of the Drawings]

[0039]

[Drawing 1]It is a graph which shows the thermal conductivity of the Magnesium alloy in which alloy composition differs.

[Drawing 2]It is a graph in the stress relaxation examination of the Magnesium alloy in which alloy composition differs which shows the stress decrease amount 40 hours after the start of test.

[Drawing 3]He is a pro every 10 minutes about the compression stress added to a specimen to the test time of a stress relaxation examination.

It is the graph [TTO / graph].

[Drawing 4]It is the Photograph substituted for drawing in which the metal texture of a Mg-3 mass %Cu-1 mass % Ca alloy (#01) is shown.

[Drawing 5]It is the Photograph substituted for drawing in which the metal texture of a Mg-3 mass %Cu-1 mass %Ca-0.1 mass %Ag (#02) alloy is shown.
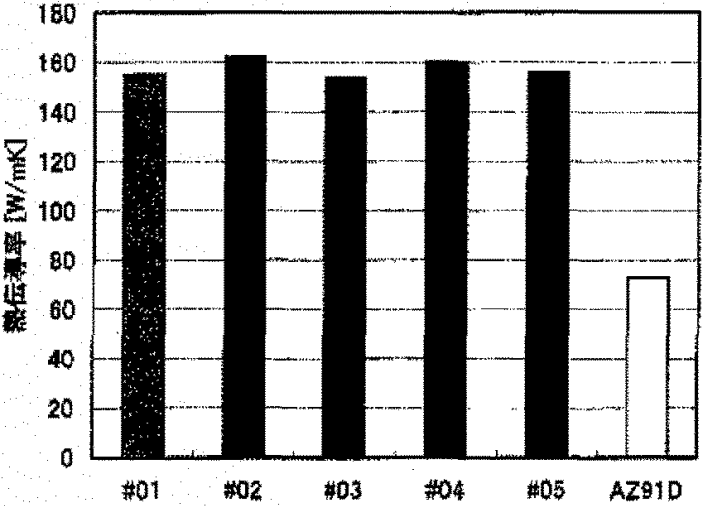
[Drawing 6]It is the Photograph substituted for drawing in which the metal texture of a Mg-3 mass %Cu-1 mass %Ca-1 mass %Ag (#03) alloy is shown.
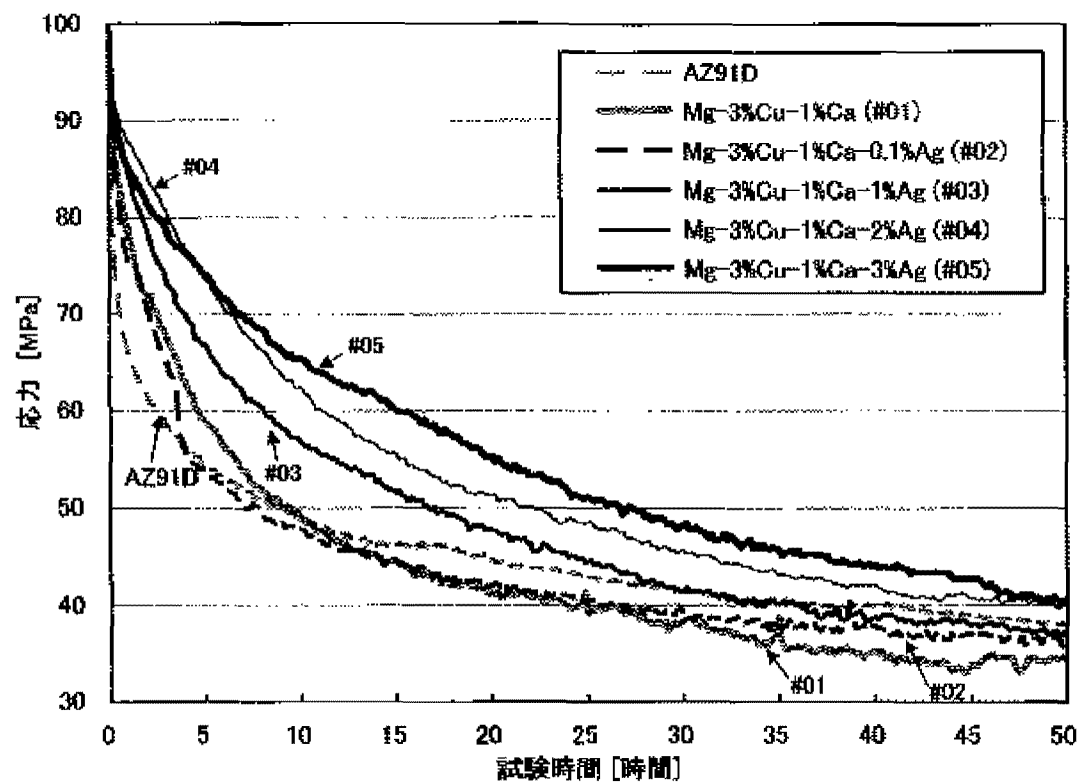
[Drawing 7]It is the Photograph substituted for drawing in which the metal texture of a Mg-3 mass %Cu-1 mass %Ca-2 mass %Ag (#04) alloy is shown.

[Drawing 8]It is the Photograph substituted for drawing in which the metal texture of a Mg-3 mass %Cu-1 mass %Ca-3 mass %Ag (#05) alloy is shown.
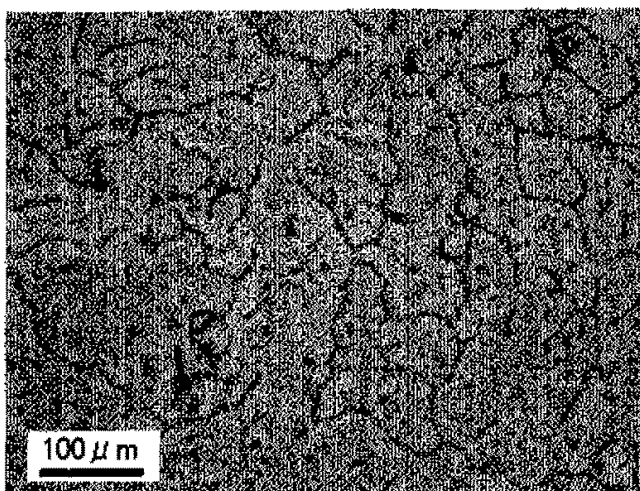
DRAWINGS

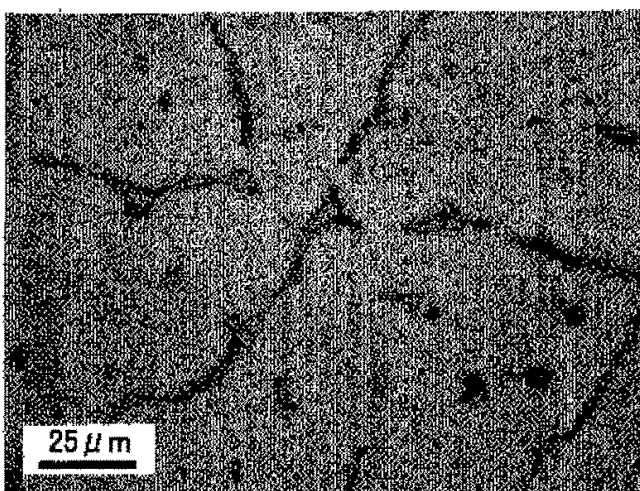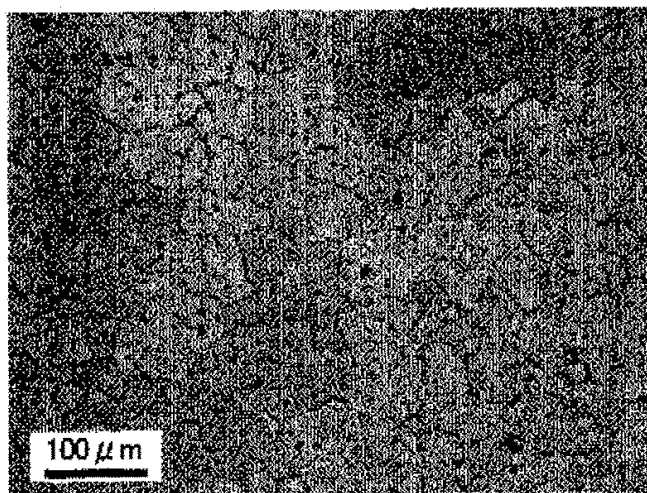[Drawing 1]

[Drawing 2]

[Drawing 3]

(a) #01 : Mg-3%Cu-1%Ca
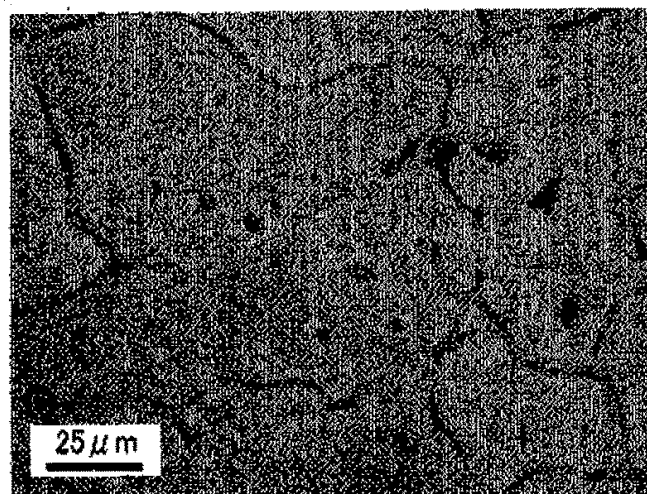

100 μm

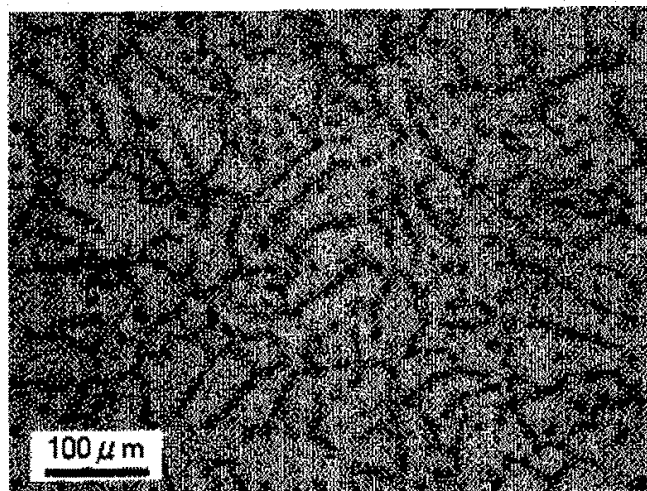(b) #01 : Mg-3%Cu-1%Ca

25 μm
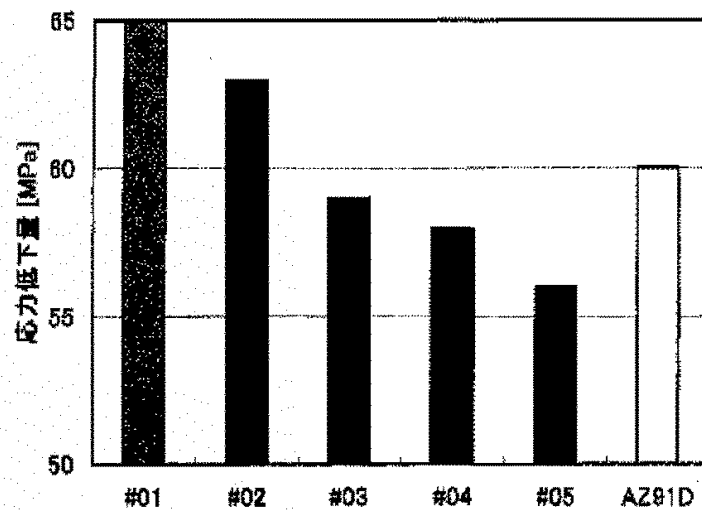
[Drawing 5]

(a) #02 : Mg-3%Cu-1%Ca-0.1%Ag

100 μm

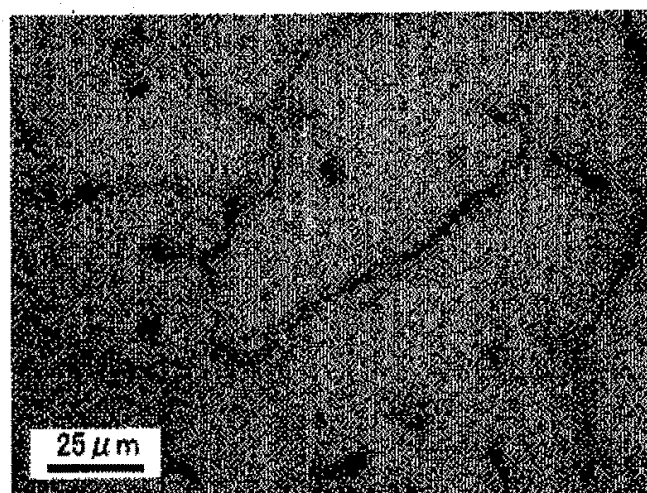(b) #02 : Mg-3%Cu-1%Ca-0.1%Ag

25 μm

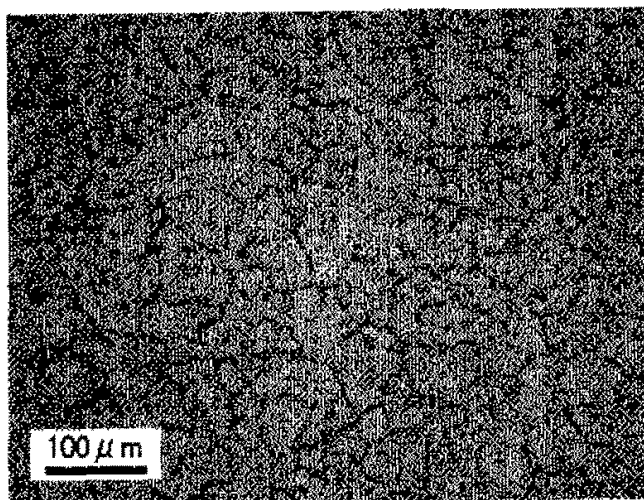(a) #03 : Mg-3%Cu-1%Ca-1%Ag

100 μm
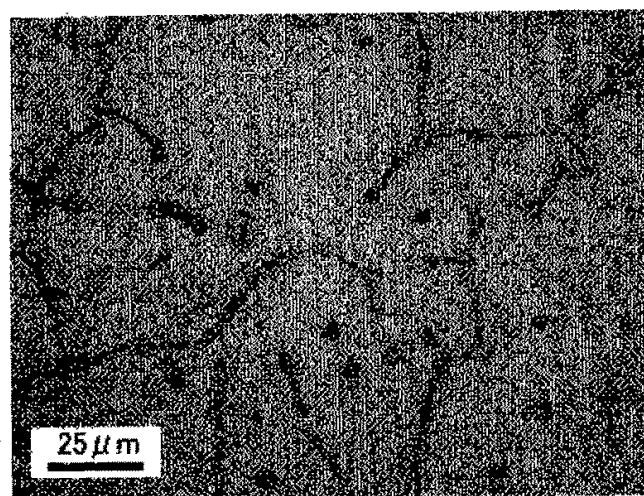
(b) #03 : Mg-3%Cu-1%Ca-1%Ag

25 μm

[Drawing 7]

(a) #04 : Mg-3%Cu-1%Ca-2%Ag

100μm
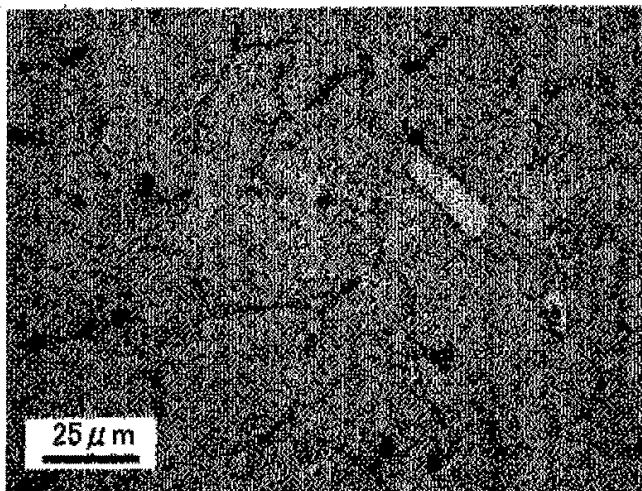
(b) #04 : Mg-3%Cu-1%Ca-2%Ag

25μm

[Drawing 8]

(a) #05 : Mg-3%Cu-1%Ca-3%Ag

100 μm

(b) #05 : Mg-3%Cu-1%Ca-3%Ag

25 μm

(54)MAGNESIUM ALLOY ROLLED MATERIAL AND METHOD FOR MANUFACTURING THE SAME

(57)Abstract

PROBLEM TO BE SOLVED: To provide a rolled material of a precipitation hardening type magnesium alloy sufficient in strength and moldability, and a method for manufacturing the rolled material of the precipitation hardening type magnesium alloy sufficient in strength and moldability.

SOLUTION: The rolled material of a magnesium alloy including 50 mass% or more of magnesium, 3.0-10.0 mass% of zinc and 0.3-3.0 mass% of zirconium and having a crystal structure of a hexagonal closest packing (hcp) structure has a pole density peak of 10° or more and -10° or less in a pole density distribution curve of a c axis of the hexagonal closest packing structure measured at ± 75° of an inclination angle from a normal direction of a rolled surface to a rolled direction.

CLAIMS

[Claim(s)]

[Claim 1]

It is the Magnesium alloy rolled stock whose crystal structure is hexagonal-closest-packing structure (hcp) including magnesium more than the 50 mass %, zinc of the 3.0 - 10.0 mass %, and a zirconium of the 0.3 - 3.0 mass %,

in a pole density distribution curve of c axis of hexagonal-closest-packing structure measured in the range whose angle of inclination from a rolling face normal line direction to a rolling direction is plus-or-minus 75degree -- a peak of pole density -- 10 degrees or more -- or

-Magnesium alloy rolled stock in 10 degrees or less.

[Claim 2]

The Magnesium alloy rolled stock according to claim 1, wherein a peak of the aforementioned pole density is in 15 degrees or more or -15 degrees or less.

[Claim 3]

The Magnesium alloy rolled stock according to claim 1 or 2 0.1 mass %-1.5 mass % Containing calcium.

[Claim 4]

A process which a crystal structure prepares a magnesium component which is hexagonal-closest-packing structure (hcp) including magnesium more than the 50 mass %, zinc of the 3.0 - 10.0 mass %, and a zirconium of the 0.3 - 3.0 mass %,

A process of performing asymmetric rolling to the aforementioned Magnesium alloy component at rolling temperature of 440 degrees C or more, and 50% or more of a bottom rate of total pressure,

****** -- a manufacturing method of Magnesium alloy rolled stock characterized by things.

[Claim 5]

A process of performing solution treatment at temperature between 380 degrees C - 520 degrees C after performing the aforementioned asymmetric rolling,

A process of performing aging treatment at temperature between 120 degrees C - 250 degrees C after performing the solution treatment,

A manufacturing method of the containing Magnesium alloy rolled stock according to claim 4.

[Claim 6]

A manufacturing method of the Magnesium alloy rolled stock according to claim 5 further including a process of press-forming between the aforementioned solution

treatment and the aforementioned aging treatment.

[Claim 7]

Magnesium alloy rolled stock of a description to any one of the Claims 4-6, wherein the aforementioned magnesium component 0.1 mass %-1.5 mass % Contains calcium further.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Field of the Invention]

[0001]

The present invention relates to the manufacturing method of the Magnesium alloy rolled stock which has the moldability which was high strength and excellent, and Magnesium alloy rolled stock, and relates to precipitation-strengthening type Magnesium alloy rolled stock which has the moldability which was especially high strength and excellent, and a manufacturing method for the same.

[Background of the Invention]

[0002]

Magnesium is the lightest-weight metal in practical use metal, has high specific strength and is further excellent also in cutting ability, vibration suppression nature, electromagnetic-shielding nature, dent-proof nature, and recycling efficiency. For this reason, the Magnesium alloy which carries out the main component of the magnesium is used for the broad purpose containing autoparts, such as electronic devices, such as a housing of a mobile phone and a notebook sized personal computer, and a tire wheel.

[0003]

However, there is a problem that the rolled stock (expansion material) of a Magnesium alloy has a low moldability (processability). This originates in forming bottom surface texture, if the crystal structure of almost all Magnesium alloys being hexagonal-closest-packing structure (hcp) and strip processing are performed. Bottom surface texture is the texture where the surface which is a bottom surface of hexagonal-closest-packing structure (0001) carried out orientation in parallel with a rolling face, and the texture whose c axis (<0001>axes) in other words carried out orientation to the normal line direction of the rolling face.

[0004]

A moldability (processability) and strength have a relation of a trade-off generally. Although a moldability can be improved by decreasing bottom surface texture also in a Magnesium alloy, if bottom surface texture decreases in number, strength will usually be deteriorated.

[0005]

A Magnesium alloy can be divided roughly into two, a solid-solution-strengthening type alloy like AZ system alloy which has obtained strength mainly by solid solution strengthening, and a precipitation-strengthening type alloy, for example like ZK system alloy which has obtained strength mainly by precipitation strengthening (or

precipitation hardening), for example.

[0006]

The Patent document 1 is disclosing applying asymmetric rolling to AZ system alloy, and obtaining the magnesium alloy material which combines strength and a moldability. In 1 set of rolls of being arranged up and down, for example, asymmetric rolling is a rolling method which changes the peripheral speed of one roll with the peripheral speed of the roll of another side, and rolls by passing between these two rolls.

The Patent document 2 is disclosing obtaining the Magnesium alloy rolled stock which a crystal structure applies asymmetric rolling to the Magnesium alloy which is hexagonal-closest-packing structure (hcp), and has high strength, and was excellent in the moldability.

[Citation list]

[Patent literature]

[0007]

[Patent document 1] Japanese Published Patent Application No. 2010-202898 (JP2010-202898A)

[Patent document 2] Japanese Published Patent Application No. 2011-058054 (JP2011-058054A)

[Summary of Invention]

[Problem to be solved by the invention]

[0008]

A precipitation-strengthening type Magnesium alloy (it is also called a "precipitation-hardening type Magnesium alloy") is advantageous in many cases, in order to be able to obtain high strength easily and to obtain a high strength material from the ability of strength to be obtained with a sludge rather than a solid-solution-strengthening type Magnesium alloy generally for this reason.

However, the Patent document 1 for solid-solution-strengthening type AZ alloy a Patent document 2, There was a case where the obtained rolled stock was [desired strength and a desired moldability] incompatible even if it applies the conditions which a Patent document 1 and a Patent document 2 disclose to a precipitation-hardening type Magnesium alloy, since it is aimed at the broad Magnesium alloy containing both of solid-solution-strengthening type and precipitation-strengthening types.

[0009]

Then, this application aims at providing the rolled stock of a precipitation-hardening type Magnesium alloy which has sufficient strength and sufficient moldability, and providing the manufacturing method of the rolled stock of a precipitation-hardening

type Magnesium alloy which has sufficient strength and sufficient moldability.

[Means for solving problem]

[0010]

The modes 1 of the present invention Magnesium more than the 50 mass %, and the zinc of the 3.0 - 10.0 mass %, It is the Magnesium alloy rolled stock whose crystal structure is hexagonal-closest-packing structure (hcp) including the zirconium of the 0.3 - 3.0 mass %, In the pole density distribution curve of the c axis of the hexagonal-closest-packing structure measured in the range whose angle of inclination from a rolling face normal line direction to a rolling direction is plus-or-minus 75degree, it is Magnesium alloy rolled stock, wherein the peak of pole density is in 10 degrees or more or -10 degrees or less.

[0011]

The modes 2 of the present invention is the Magnesium alloy rolled stock of a description in the modes 1, wherein the peak of the aforementioned pole density is in 15 degrees or more or -15 degrees or less.

[0012]

0.1 mass %-1.5 mass % The modes 3 of the present invention is the Magnesium alloy rolled stock of a description in the containing modes 1 or 2 about calcium.

[0013]

The modes 4 of the present invention Magnesium more than the 50 mass %, and the zinc of the 3.0 - 10.0 mass %, The process which a crystal structure prepares the magnesium component which is hexagonal-closest-packing structure (hcp) including the zirconium of the 0.3 - 3.0 mass %, It is a manufacturing method of Magnesium alloy rolled stock including the process of performing asymmetric rolling at the rolling temperature of 440 degrees C or more, and 50% or more of the bottom rate of total pressure in the aforementioned Magnesium alloy component.

[0014]

The process of performing solution treatment at the temperature between 380 degrees C - 520 degrees C after the modes 5 of the present invention performs the aforementioned asymmetric rolling, After performing the solution treatment, it is a manufacturing method of the Magnesium alloy rolled stock of a description in the modes 4 further including the process of performing aging treatment at the temperature between 120 degrees C - 250 degrees C.

[0015]

The modes 6 of the present invention is a manufacturing method of the Magnesium alloy rolled stock of a description in the modes 5 further including the process of

press-forming between the aforementioned solution treatment and the aforementioned aging treatment.

[0016]

Magnesium alloy rolled stock described in any of the modeses 4-6 to which the modes 7 of the present invention is characterized by 0.1 mass %-1.5 mass % The aforementioned magnesium component containing calcium further. It comes out.

[Effect of the Invention]

[0017]

In the invention in this application, it is considered as one thing of the characteristics which asymmetric rolling of 50% or more of the bottom rate of total pressure is performed for a precipitation-strengthening type Magnesium alloy at 440 degree-C or more temperature, and is acquired for rolled stock. Thus, in the pole density distribution curve of the c axis, as for the obtained Magnesium alloy rolled stock, the peak of pole density will be 10 degrees or more or -10 degrees or less.

It becomes possible to provide the rolled stock of a precipitation-hardening type Magnesium alloy which has sufficient strength and sufficient moldability by this, and to provide the manufacturing method of the rolled stock of a precipitation-hardening type Magnesium alloy which has sufficient strength and sufficient moldability.

[Brief Description of the Drawings]

[0018]

[Drawing 1]Fig.1 is a schematic cross section which describes asymmetric rolling.

[Drawing 2]Fig.2 is a pole figure of 1 - 1 sample of working examples.

[Drawing 3]Fig.3 is a pole figure of 1 - 1 sample of comparative examples.

[Drawing 4]The pole density distribution curve of the start material of ZK60, 1 - 1 sample of working examples, and 1 - 1 sample of comparative examples is shown.

[Drawing 5]The pole density distribution curve of the start material of ZK60, 2 - 1 sample of working examples, and 2 - 1 sample of comparative examples is shown.

[Drawing 6]The pole density distribution curve of the start material of AZ31, 5 - 1 sample of comparative examples, and 5 - 3 samples of comparative examples is shown.

[Drawing 7]Fig.7 shows the pole density distribution curve of the start material of AZ31, 4 - 1 sample of comparative examples, and 4 - 3 samples of comparative examples.

[Drawing 8]The texture observation result of ZK60 material is shown. Fig.8 (a) is an observation-by-optical-microscope result of ZK60 start material, Fig.8 (b) is an observation-by-optical-microscope result of 1 - 1 sample of working examples, Fig.8 (c) is an observation-by-optical-microscope result of 2 - 1 sample of working examples, and Fig.8 (d) is a SEM observation result of 2 - 1 sample of working examples.

[Drawing 9]The texture observation result of AZ31 material is shown. Fig.9 (a) is an observation-by-optical-microscope result of AZ31 start material, Fig.9 (b) is an observation-by-optical-microscope result of 5 - 3 samples of comparative examples, and Fig.9 (c) is an observation-by-optical-microscope result of the comparative example 4-3.

[Drawing 10]The texture observation result by SEM of ZK60 material is shown. Fig.10 (a) is a SEM observation result of the sample which performed solution treatment and aging treatment to 2 - 1 sample of working examples, and is Fig.10 (b).

It is a SEM observation result of the sample which performed solution treatment and aging treatment to 3 samples of comparative examples, and Fig.10 (c) shows the SEM observation result to which the black frame part of Fig.10 (a) was expanded.

[Drawing 11]The form and the dimension of the specimen used for the tensile test are shown.

[Drawing 12]It is a graph which shows a tensile test result, and Fig.12 (a) shows proof stress 0.2%, and Fig.12 (b) shows a stretch.

[Drawing 13]It is a schematic view of a molding testing machine.

[Drawing 14]Are a photograph to illustrate the sample evaluation result after a molding examination, and Fig.14 (a), An evaluation result shows 2 - 1 sample of working examples after the molding examination which made retention temperature of the specimen 100 degrees C which were "x", and them Fig.14 (b), 3 samples of comparative examples after the molding examination which made retention temperature of the specimen 150 degrees C whose evaluation result was "**" are shown, and Fig.14 (c) shows 2 - 1 sample of working examples after the molding examination which made retention temperature of the specimen 125 degrees C whose evaluation result was "O."

[Description of Embodiments]

[0019]

Hereinafter, based on Drawings, the embodiment of the present invention is described in detail. although the term (for example, -- "the upper" -- "-- another term including lower", the "right", the "lefts", and those terms) which shows a specific direction and position if needed is used in the following descriptions, It is for use of those terms making easy an understanding of invention which referred to Drawings, and technical scope of the present invention is not limited by those definitions.

[0020]

An inventor of the present application a precipitation-strengthening type Magnesium alloy by performing asymmetric rolling of 50% or more of the bottom rate of total pressure at the temperature of 440 degrees C or more so that details may be mentioned below, The orientation of the c axis (<0001>axes) of the rolled stock which might have

hexagonal-closest-packing structure is shown, what (that is, the position of a peak is 15 degrees or more or -15 degrees or less) the peak of a pole density distribution curve shifts 10 degrees or more from 0 degree (namely, -- the position of a peak is 10 degrees or more or -10 degrees or less), preferable shifts 15 degrees or more from 0 degree for was found out.

[0021]

As for this, the orientation of c axis means 10 degrees or more, preferably that 15 degrees or more lean from a normal line direction to the rolling direction or rolling opposite direction of a rolling face.

And the state (that is, the position of a peak is 10 degrees or more or -10 degrees or less) where the peak of the pole density distribution curve shifted 10 degrees or more of precipitation-strengthening type Magnesium alloy **** concerning the invention in this application from 0 degree is maintained even if it performs solution treatment and aging treatment.

[0022]

Therefore, after performing asymmetric rolling, the more outstanding moldability is realizable by performing solution treatment. And after processing it into desired form, by performing aging treatment, a sludge can be deposited and material strength can be made sufficient high. As mentioned above, the Magnesium alloy rolled stock of the invention in this application which 10 degrees or more of peaks of a pole density distribution curve have shifted from 0 degree can secure sufficient high ductility (and toughness) required [reaching strongly] by aging treatment.

That is, the Magnesium alloy rolled stock concerning the invention in this application is [sufficient strength and sufficient moldability] compatible.

[0023]

Although the details of the invention in this application are described below, it describes about a pole density distribution curve indispensable to understand the present invention first.

[0024]

1. Pole density distribution curve

How to search for a pole density distribution curve is described.

First, it asks for the pole figure of a surface (0002) using the reflection method of most general Schulz as an appraisal method of crystal orientation, such as texture, by X-ray diffraction.

As for the alpha angle in the case of measurement of a pole figure, it is desirable to consider it as the range of 15 degrees - 90 degrees from the peripheral circle of a pole

figure so that the outline of reflection intensity distribution can grasp clearly. As for measurement, it is preferable to perform an alpha angle and a beta angle every 3-10 degrees like [in every 5 degrees]. It is because there is a possibility that measurement accuracy may be deteriorated when larger than 10 degrees, and measuring time will be required more than needed if smaller than 3 degrees.

[0025]

Fig.2 is a pole figure of 1 - 1 sample of working examples which mention details below, and Fig.3 is a pole figure of 1 - 1 sample of comparative examples which mention details below.

These use the method of presentation of general stereographic projection as a pole figure of rolled stock. As shown in the figure, the topmost part of a circular stereographic projection surface shows RD (rolling direction), and, in -RD (rolling opposite direction), the bottom shows. Although not described into the figure, ND (rolling face normal line direction) takes the lead in a surface of projection. And the pole density of the surface (0002) of the X-rays corresponding to various alpha angles and beta angles observed [direction] has appeared in the shape of a contour line in the figure, and it is the value which **(ed) (0002) diffraction intensity in the applicable position with (0002) the diffraction intensity of the powder sample of non-orientation. Therefore, the value of the pole density 1 shows the pole density like the method of random.

[0026]

In this Description, RD and -RD are setting -RD (rolling opposite direction) and the outlet side of rolling to RD (rolling direction) for the entrance side of rolling. Since direction of shearing stress becomes opposite about the sample which performed asymmetric rolling in the rolling face on the early roll side of peripheral speed, and the rolling face on the roll side with a slow peripheral speed, the pole figure obtained from the mutual surface serves as a relation which turned over and replaced the upper and lower sides. Then, in this Description, a pole figure shall be obtained from the rolling face on the quick roll side of peripheral speed (surface which ground this).

[0027]

However, even if it obtains a pole figure from the rolling face on the late roll side of peripheral speed, without making a mistake in comparing and understanding in which, Since it is in above-mentioned relation, the pole density distribution curve to be described from now on can be acquired, and an equivalent result can be obtained about the shift amount (gap from 0 degree which is a center value) of the peak which is the characteristic value.

[0028]

Next, a pole density distribution curve is acquired from the obtained pole figure. The measurement result of a pole density distribution curve is illustrated. The pole density distribution curve of 1 - 1 sample of working examples shown in Fig.4 is acquired using the data of the pole figure shown in above-mentioned Fig.2, and the pole density distribution curve of 1 - 1 sample of comparative examples in Fig.4 is acquired using the data of the pole figure shown in above-mentioned Fig.3.

[0029]

the horizontal axis of a graph on which a pole density distribution curve is shown is an angle of inclination from ND (normal of a rolling face), and pass ND (the center of a stereo surface) from -RD in a pole figure (stereo surface) -- it corresponds to the position on the straight line which results in RD. And an angle of inclination is negative, expresses the -RD side, and shows the RD side by positive.

On the other hand, the vertical axis of the graph which shows a pole density distribution curve is the pole density of the position where a pole figure corresponds.

[0030]

Thus, the pole density distribution searched for is vertical to the cross direction of rolled stock, and the angle of inclination to ND shows the pole density of the c axis which is theta.

[0031]

As for a pole density distribution curve, in order to clarify the overview, it is preferable to display -75 degree-+75 degree (from ND to namely, the direction of RD **75 degrees) of a pole figure time base range. And this is realizable because an alpha angle shall be 15 degrees - 90 degrees in measurement of an above-mentioned pole figure.

[0032]

Development of bottom surface texture will observe a peak with sharp pole density to the neighborhood whose angle of inclination is 0 degree. On the other hand, if bottom surface texture machines decrease in number, according to the form of the reduction, the shift of the peak to the position where the angle of inclination separated from 0 degree, blow donning of a peak, the appearance of a double peak, etc. will take place. Therefore, it becomes possible by acquiring a pole density distribution curve to grasp some of bottom surface texture quantitatively.

[0033]

2. Asymmetric rolling It describes about the asymmetric rolling of the present invention below.

Fig.1 is a schematic cross section which describes asymmetric rolling. The rolling roll of

the lot which consists of the roll 1 and the roll 2 is arranged, and the magnesium alloy material 3 passes the meantime and it is rolled. According to the embodiment shown in Fig.1, peripheral speed of the roll 1 is made quicker than the peripheral speed of the roll 2 by enlarging the diameter of the roll 1 rather than the diameter of the roll 2, and rotating the roll 1 and the roll 2 at the same revolving speed (angular velocity). The rolls 1 and 2 rotate in the direction shown by a white arrow in the figure, respectively.

[0034]

Of course, the method of making peripheral speed of the roll 1 quicker than the peripheral speed of the roll 2 is not limited to this, it can make the roll 1 and the roll 2 the same diameter, for example, and any method known from the former, such as making revolving speed of the roll 1 high, can be used for it.

[0035]

Shearing stress can be made to act on rolled stock by performing asymmetric rolling. By the quick roll 1 side of peripheral speed, shearing stress is received more in details in the rolling direction of the magnesium alloy material 3 shown with the black arrow in the figure (RD), i.e., the right of Fig.1. On the other hand, in the late roll 2 side of peripheral speed, shearing stress is received in the rolling opposite direction of a rolling direction and a 180-degree counter direction (-RD), i.e., the left of Fig.1.

[0036]

The vertical bar in the magnesium alloy material 3 shows typically the influence on the rolled stock by this shearing stress. The vertical vertical bar virtually pulled to the magnesium alloy material before asymmetric rolling turns into a line of the slant which the roll 1 side shifted in the direction of RD, and the roll 2 side shifted in the direction of -RD, when shearing stress is added as mentioned above by asymmetric rolling.

[0037]

In the asymmetric rolling concerning the present invention, the rolling temperature of 440 degrees C or more and the bottom rate of total pressure are made into 50% or more. Thereby, in the pole density distribution curve of c axis, it becomes possible to shift reliably 10 degrees or more of peaks of pole density from 0 degree.

Preferably, rolling temperature is 470 degrees C or more. The moldability which was more excellent in thereby more high strength can be obtained.

Rolling temperature is 550 degrees C or less preferably. It is because rolling temperature may exceed and carry out liquation of the solidus line if it exceeds 550 degrees C.

[0038]

With the rolling temperature as used in [since it is very difficult the temperature of the

material under processing, and to especially measure the temperature of the magnesium alloy material under rolling in practice] this Description, It sets like a roll turner, heats just before strip processing, and means the heating temperature (or arrival temperature) of the material at the time of the aforementioned heating at the time of rolling succeedingly (without making it delayed intentionally).

[0039]

When only an one pass performs asymmetric rolling with the bottom rate of total pressure of asymmetric rolling, Meaning the rolling reduction of the one pass, a plural-passes ****** case is the rolling reduction (namely, rolling reduction for which it asks from the board thickness after performing board thickness before performing asymmetric rolling of the plural passes concerned, and asymmetric rolling of the plural passes concerned) of the whole plural passes about asymmetric rolling. When strip-processing nature and the amount of shear strains introduced are taken into consideration, it is preferable to make rolling reduction per one pass into 5 to 30%, and to secure the bottom rate of total pressure of 50% or more with plural passes preferably.

[0040]

Whenever it carries out one-pass rolling, rolling of such plural passes may be again heated to a predetermined rolling temperature, and may perform the following path. After heating to a predetermined rolling temperature, continuous rolling of plural passes may be performed.

[0041]

Peripheral-speed [pan] rolling and asymmetric rolling may be carried out by continuous rolling. In this case, the bottom rate of total pressure of asymmetric rolling means the rolling reduction for which it asks from change of the board thickness by asymmetric rolling.

[0042]

various kinds of materials, such as extruded materials, such as casting slab, the usual rolled stock (etc. -- peripheral-speed rolled stock), and die-casting, can be used for the material which performs asymmetric rolling. In order to remove distortion, annealing held for more than 10 minutes at the temperature of the range of 300 degrees C - 450 degrees C before performing asymmetric rolling may be performed as appropriate.

[0043]

The shift of the peak of the pole density distribution curve of the rolled stock which was 440 degrees C or more in rolling temperature about a solid-solution-strengthening type magnesium alloy material like AZ31 alloy, and was obtained, for example in many cases even if it performed asymmetric rolling with the rolled bar affair of 50% or more of the

bottom rate of total pressure is less than 10 degrees. In the case of a double peak, this says that peak of one of the two is less than 10 degrees, and does not limit the position of another peak to it.

[0044]

The precipitation-hardening type Magnesium alloy concerning the invention in this application by carrying out asymmetric rolling of the rolling temperature of 440 degrees C or more, and the bottom rate of total pressure at 50% or more. The Reason which 10 degrees or more of peaks of the pole density distribution curve of the obtained rolled stock shift. And although there are also many still obscure points about the Reason for the rolled stock concerning the invention in this application which has the peak shifted from 0 degree 10 degrees or more in this way having the moldability outstanding after solution heat treatment, and having strength sufficient after aging treatment, the mechanism which an inventor considers is as follows. However, this mechanism expected is not what meant restricting technical scope of the present invention.

[0045]

When asymmetric rolling is carried out at the elevated temperatures above 440 degrees C in the case of a solid-solution-strengthening type Magnesium alloy like AZ31, the peaks of the pole density distribution curve of the rolled stock obtained even if it compared and the bottom rate of total pressure of rolling was low are the 1st peak (main peak) and the 2nd peak (sub peak.). Usually, two peaks of the peak whose height is lower than a main peak appear, and the thing for which 10 degrees or more of second peaks are shifted -- there is it (for example, many comparative examples 4-3 etc. of the Fig.7 which mentions details below) -- however, 10 degrees or more of main peaks are not usually shifted.

It is thought of for big twinning of an azimuth change to happen easily during asymmetric rolling that the 2nd peak shifts 10 degrees or more. And since it happens at the low bottom rate of total pressure, this twinning forms the 2nd peak easily from the original bottom surface texture (the 1st peak).

Therefore, although c axis inclines, a main peak does not necessarily shift 10 degrees or more.

On the other hand, in the case of precipitation-strengthening type Magnesium alloys, such as ZK60 alloy, even if it performs asymmetric rolling at an elevated temperature, twinning does not happen easily (therefore, the peak of the pole density distribution curve of the obtained rolled stock does not separate into two). As a result, in order that slide systems, especially c+a slides other than a bottom surface slide may work in addition to a bottom surface slide, it is thought that c axis inclines gradually with the

increase in rolling reduction. And it seems by making the bottom rate of total pressure into 50% or more that a peak shifts 10 degrees or more.

Since inclination of c axis does not usually change with the recrystallization which arises during solution treatment so much, the Magnesium alloy which has hcp structure is. It is thought that it has the moldability where the bottom surface slide worked easily and which was [the time of press forming after solution heat treatment] excellent in the rolled stock which requires a peak for the invention in this application which has the texture (c axis inclined largely) which shifted largely as the result by asymmetric rolling.

[0046]

As the working example mentioned below shows details, the material strength after the rolled stock concerning the invention in this application which performed asymmetric rolling at the rolling temperature of 440 degrees C or more performs solution treatment and aging treatment compared with the rolled stock which performed peripheral-speed rolling, such as usual [with a rolling temperature of about 300 degrees C], is high.

Since it is maintained even if the precipitation under rolling since this has a high rolling temperature does not take place easily, it will be in the state where the alloying element was more mostly dissolved after rolling and this state performs solution treatment. Also after solution treatment, there are many amounts of dissolution of an alloying element, and it thinks for the quantity of the minute sludge which deposits by subsequent aging treatment to increase.

It is carrying out asymmetric rolling of the precipitation-strengthening type Magnesium alloy above 440 degrees C in the invention in this application for the above Reasons, and it is thought that the magnesium alloy sheet material which is excellent in a moldability in the solution-heat-treatment state, and has high strength in the state of prescription is obtained.

[0047]

The peripheral-speed ratios (ratio of the peripheral speed of the quicker one when peripheral speed of the later one is set to 1 among 1 set of rolls) of asymmetric rolling are 1.4-2.0 preferably. It is because big shearing stress occurs by the time of rolling, so c axis can be made to be able to incline in a rolling direction or a rolling direction, and an opposite side more easily if peripheral speed is 1.4 or more (that is, the peak of a pole density distribution curve shifts from 0 degree more easily). On the other hand, if a peripheral-speed ratio exceeds 2.0, while it will become difficult to perform rolling which becomes easy to produce the slide between material and a roll and where it was stabilized, it is because the surface disposition of material may get remarkably bad.

[0048]

Cooling after rolling may be air cooling, and may perform forced cooling, such as water cooling. Preferably, forced cooling is performed. It is because it can inhibit that a sludge will deposit by the time it is cooled by the room temperature.

[0049]

3. Solution treatment

As for the rolled stock of a precipitation-strengthening type Magnesium alloy which performed above-mentioned asymmetric rolling, it is preferable to perform solution treatment continuously. Solution treatment carries out as the main objects making the sludge which deposited by the rolling process dissolve to a matrix.

Solution treatment is preferably carried out at the temperature between 380 degrees C - 520 degrees C. It is because a sludge does not dissolve sufficiently to a matrix, but many sludges may remain, and a crystal grain may become big and rough if 520 degrees C is exceeded if a solution treatment temperature is lower than 380 degrees C.

[0050]

The retention time (time to hold after reaching a predetermined solution treatment temperature) of solution heat treatment is 1 hour - 48 hours preferably. This is because the time for diffusion is required according to a solution treatment temperature in consideration of the diffusion rate of a solute atom in order to make a solute atom dissolve sufficiently. It is preferable that the organization after solution treatment is the recrystallized structure of a homaxial grain because of next molding.

[0051]

It is preferable to quickly cool by burning underwater, for example etc. after solution treatment. It is because a sludge can be prevented from depositing during cooling.

[0052]

As mentioned above, even if it performs solution treatment, the state acquired by above-mentioned asymmetric rolling where the peak position of a pole density distribution curve has shifted 10 degrees or more from 0 degree (that is, the position of a peak is 10 degrees or more, or it is -10 degrees or less) is maintained.

[0053]

That is, the state after solution heat treatment has little sludge, and since it is in the state which bottom surface texture reduced, it is excellent with the moldability compared with the case where solution heat treatment is not performed.

[0054]

4. Molding

It molds into desired form, after performing above-mentioned asymmetric rolling (after

performing preferable further above-mentioned solution treatment).

Molding may use any forming method (or the plastic deformation method). As such a forming method, press forming (draw forming, bending molding, and stretch forming are included) can be illustrated.

Molding may be performed between the colds, if a crack does not arise, and it may be performed between ** or between heat.

[0055]

5. Aging treatment

After performing above-mentioned molding, material strength is made to increase by performing aging treatment and depositing a sludge.

Although aging treatment is based on the alloy composition mentioned below, it is preferably performed at the temperature (prescription temperature) between 120 degrees C - 250 degrees C, more preferably the temperature between 150 degrees C - 210 degrees C. It is because high strength may not be obtained that sufficient quantity of a sludge may be unable to be obtained, and it will be easy to make a sludge big and rough if prescription temperature is too high if prescription temperature is too low.

[0056]

The retention time held at an above-mentioned prescription temperature is 24 hours - 200 hours preferably, and is 48 hours - 150 hours more preferably. It is because sufficient quantity of a sludge may be unable to be obtained, and a sludge becomes big and rough if prescription time is long and high strength may not be obtained, if prescription time is short.

[0057]

Since the sludge which deposits by aging treatment depends on alloy composition, it is explained in full detail by the item of alloy composition.

[0058]

In the invention in this application, Magnesium alloy rolled stock, wherein the peak of pole density is in 10 degrees or more or -10 degrees or less has been obtained by performing above-mentioned asymmetric rolling.

And the state where the peak of pole density is in 10 degrees or more or -10 degrees or less is maintained after solution treatment (i.e., before molding). If it does not mold after solution treatment, this state is maintained even aging treatment of after.

[0059]

Therefore, rolled stock immediately after the Magnesium alloy rolled stock concerning the invention in this application performs asymmetric rolling is a concept which contains the rolled stock by which solution treatment was carried out, the molded rolled

stock, and the rolled stock by which aging treatment was carried out from the first.

[0060]

6. Alloy composition

The precipitation-strengthening type Magnesium alloy used for the Magnesium alloy rolled stock concerning the present invention described above, it is a Magnesium alloy which carries out the main component of the magnesium (Mg) (namely, -- more than the 50 mass % contains magnesium), and contains the zinc (Zn) of the 3.0 - 10.0 mass %, and the zirconium (Zr) of the 0.3 - 3.0 mass %.

[0061]

The Magnesium alloy used for the Magnesium alloy rolled stock concerning the present invention has such composition. and a crystal structure is hexagonal-closest-packing structure (hcp).

By and the thing for which above-mentioned asymmetric rolling is performed to the Magnesium alloy which has such composition and a crystal structure, In the pole density distribution curve of c axis measured in the range whose angle of inclination from a rolling face normal line direction to a rolling direction is plus-or-minus 75degree, the peak of pole density is 10 degrees or more or -10 degrees or less.

[0062]

Zinc has an effect of improvement in strength, corrosion resistance, and fluidity, if it is less than the 3.0 mass %, it may not have these effects, and if larger than the 10.0 mass %, a Mg-Zn system intermetallic compound may exist so much.

in order to acquire the above-mentioned effect more reliably, a zincky quantity is the 4.0 to 7.0 mass %, and also is the 4.8 to 6.2 mass % more preferably.

The composition shown in this paragraph eye "6. alloy composition" is the average composition of the whole material, and does not mean local composition.

[0063]

a zirconium has an effect of a grain-refining and hot-working disposition top, if it is less than the 0.3 mass %, these effects may not be sufficient, and if larger than the 3.0 mass %, it may become excessive [a Zn-Zr system intermetallic compound or Zr solid solution]. in order to acquire the above-mentioned effect more reliably, the quantity of a zirconium is the 0.4 to 2.0 mass %, and also is the 0.5 to 1.5 mass % more preferably.

[0064]

Mg_4Zn_7 (beta$_1$' phase) and Zn_2Zr can be illustrated, for example as a sludge at the time of performing aging treatment to the Magnesium alloy concerning the invention in this application which has such composition.

[0065]

As a Magnesium alloy which has such composition, for example The zinc of the 3.0 - 10.0 mass %, The Magnesium alloy which the remainder becomes from the element (for example, impurity) of others below the 1.0 mass % in magnesium and the sum total can be mentioned including the zirconium of the 0.3 - 3.0 mass %.

[0066]

However, the Magnesium alloy used for the invention in this application is not limited to **. Contain magnesium (Mg) more than the 50 mass %, the zinc (Zn) of the 3.0 - 10.0 mass %, and the zirconium (Zr) of the 0.3 - 3.0 mass %, and if a crystal structure is hexagonal-closest-packing structure (hcp), Even if other elements of any are further included, the moldability excellent in the peak of pole density considering it as 10 degrees or more or -10 degrees or less by asymmetric rolling and high strength may be made compatible.

[0067]

The following can be illustrated as an effective addition amount of such other elements of any and the element concerned.

- Ca

Ca has an effect of fireproofness nature. This effect can be reliably acquired by making an addition amount into the 0.1 mass % - the 1.5 mass %.

[0068]

Any elements other than Ca may be included for an improvement of various kinds of characteristics of the Magnesium alloy concerning the invention in this application.

[Working example]

[0069]

1. Working example 1

- Start material

Table 1 shows composition of the start material of two alloys used for obtaining the working example and comparative example sample which are explained in full detail below, ZK60A (hereinafter referred to as " ZK60 "), and AZ31B (henceforth "AZ31").

as start material, the rolled stock (etc. -- peripheral-speed rolled stock) of marketing 3mm in thickness was used.

[0070]

[Table 1]

	Ａｌ	Ｚ ｎ	Ｚ ｒ	Ｍ ｎ	Ｆ ｅ	Ｓ ｉ	Ｃ ｕ	他	Ｍ ｇ
ZK60A		4.8〜6.2 標準値 5.5	>0.45 標準値 0.6					<0.3	残部
AZ31B	2.70	1.10		0.42	0.003	0.02	<0.01	<0.3	残部

（質量%）

[0071]

- Rolling

Rolled stock was performed using the above-mentioned start material. The rolled bar affair of each sample is shown in Table 2.

Asymmetric rolling was performed using the rolling roll shown in Fig. 1. The diameter of the roll 1 is 144 mm and the diameter of the roll 2 is 96 mm. Asymmetric rolling of the peripheral-speed ratio 1.5 was performed by rotating the roll 1 and the roll 2.

The rolling reduction of an one pass is about 10%, and obtained the bottom rate of total pressure (total rolling reduction) which performs asymmetric rolling of plural passes and is shown in Table 2.

[0072]

****** rolling was performed using the roll of 1 set of 150-mm diameter. The rolling reduction of an one pass is about 10%, and obtained 70% of bottom rate of total pressure which performs peripheral-speed rolling, such as plural passes, and is shown in Table 2.

[0073]

[Table 2]

サンプル	スタート材 （合金種別）	圧延種別	圧延温度（℃）	トータル圧 下率（％）
実施例 1 － 1	ＺＫ６０	異周速圧延	４５０	７０
実施例 1 － 2	ＺＫ６０	異周速圧延	４５０	５０
比較例 1 － 1	ＺＫ６０	異周速圧延	４５０	３０
比較例 1 － 2	ＺＫ６０	異周速圧延	４５０	２０
実施例 2 － 1	ＺＫ６０	異周速圧延	５００	７０
実施例 2 － 2	ＺＫ６０	異周速圧延	５００	５０
比較例 2 － 1	ＺＫ６０	異周速圧延	５００	３０
比較例 2 － 2	ＺＫ６０	異周速圧延	５００	２０
比較例 3	ＺＫ６０	等周速圧延	３００	７０
比較例 4 － 1	ＡＺ３１	異周速圧延	４５０	７０
比較例 4 － 2	ＡＺ３１	異周速圧延	４５０	５０
比較例 4 － 3	ＡＺ３１	異周速圧延	４５０	３０
比較例 5 － 1	ＡＺ３１	異周速圧延	３００	７０
比較例 5 － 2	ＡＺ３１	異周速圧延	３００	５０
比較例 5 － 3	ＡＺ３１	異周速圧延	３００	３０
比較例 5 － 4	ＡＺ３１	異周速圧延	３００	２０
比較例 6	ＡＺ３１	等周速圧延	３００	７０

[0074]

- Heat treatment

The sample (the working example 1-1, the working example 1-2, the comparative example 1-1, the comparative example 1-2, the working example 2-1, the working example 2-2, the comparative example 2-1, the comparative example 2-2, and the comparative example 3) whose alloy classification is ZK60 performed aging treatment for 96 hours at 180 degrees C, after performing solution treatment for 24 hours at 400 degrees C.

On the other hand, the sample (the comparative example 4-1 to 4-3, the comparative example 5-1 to 5-4 wearing comparative example 6) whose alloy classification is AZ31 performed annealing (annealing) for 30 minutes at 300 degrees C.

[0075]

- Measurement of a pole density distribution curve

About the sample after start material and rolling, the pole density distribution curve was also searched for by the method shown below.

[0076]

First, it asked for (0001) the pole figure of each sample with the reflection method of

Schulz. The sample (25 mm x 25 mm) was cut out from each sample, and this sample was measured using the sample which carried out final polishing by #2000, after deleting board thickness to a half degree with waterproof emery paper. About the sample which performed asymmetric rolling, the surface on the quick roll side of peripheral speed was deleted and ground, and it was considered as the measuring plane.

[0077]

The pole figure was created in alpha= 15 degrees - 90 degrees. The degree of angle of diffraction made near the theoretical angle scan, and used the angle for which it asked by the full-width-at-half-maximum middle point method. Although the measurement angle of the background was based on the degree of angle of diffraction of **2 degrees, since it lapped with other diffraction lines partially, it was made into angle-of-diffraction degree-2 degree of (10-10), and the degree of angle of diffraction of +2 degrees of (10-11). Background correction and strength correction by the spot sample which used pure Mg powder were performed to the obtained diffraction intensity, and the pole figure was obtained. The terms and conditions about measurement are shown in Table 3.

[0078]

[Table 3]

Ｓｃｈｕｌｚの反射法測定条件

Ｘ線源	ＣｕＫα線
シュルツスリット	１ｍｍ
発散スリット	１°
α走査範囲	１５°～９０°
β走査範囲	０°～３６０°
αステップ幅	５°
βステップ幅	５°
γ振動幅	５ｍｍ

[0079]

Based on (0001) the obtained pole figure, the pole density distribution curve of the range of **75-degree angle of inclination from -RD to RD through ND was created.

The pole figure measured to Fig.2 and 3 is illustrated. Fig.2 is a pole figure of 1 - 1 sample of working examples, and Fig.3 is a pole figure of 1 - 1 sample of comparative examples.

[0080]

A pole density distribution curve is illustrated to Fig.4 - Fig.7. Fig.4 shows the pole density distribution curve of the start material of ZK60, 1 - 1 sample of working examples, and 1 - 1 sample of comparative examples. Fig.5 shows the pole density distribution curve of the start material of ZK60, 2 - 1 sample of working examples, and 2 - 1 sample of comparative examples. Fig.6 shows the pole density distribution curve of the start material of AZ31, 5 - 1 sample of comparative examples, and 5 - 3 samples of comparative examples. Fig.7 shows the pole density distribution curve of the start material of AZ31, 4 - 1 sample of comparative examples, and 4 - 3 samples of comparative examples.

[0081]

Thus, it asks for the pole density curve of each sample, and the position of the peak is shown in Table 4. Like the comparative example 4-1 of Fig.7, when two peaks were accepted, the position of the peak with higher height was made into the peak position of the sample concerned.

[0082]

[Table 4]

サンプル	状態	ピーク位置（°）
ＺＫ６０スタート材	スタート材	5
ＡＺ３１スタート材	スタート材	5
実施例１－１	圧延後	－２０
実施例１－２	圧延後	－１０
比較例１－１	圧延後	－５
比較例１－２	圧延後	0
実施例２－１	圧延後	－１５
実施例２－２	圧延後	－１０
比較例２－１	圧延後	－５
比較例２－２	圧延後	0
比較例３	圧延後	７．５
比較例４－１	圧延後	0
比較例４－２	圧延後	0
比較例４－３	圧延後	0
比較例５－１	圧延後	0
比較例５－２	圧延後	0
比較例５－３	圧延後	0
比較例５－４	圧延後	0
比較例６	圧延後	0

[0083]

As shown in Table 4, each working-example sample has a peak of pole density in 10 degrees or more or -10 degrees or less, and the shift amount (gap from 0 degree) of the peak has become 10 degrees or more. On the other hand, each of start material and comparative example samples is, while the peak of pole density is -5 degree-7.5 degree, and the shift amount of the peak has become less than 10 degrees.

[0084]

- Metal texture observation

Fig.8 shows the texture observation result of ZK60 material. Fig.8 (a) is an

observation-by-optical-microscope result of ZK60 start material, Fig.8 (b) is an observation-by-optical-microscope result of 1 - 1 sample of working examples, Fig.8 (c) is an observation-by-optical-microscope result of 2 - 1 sample of working examples, and Fig.8 (d) is a SEM observation result of 2 - 1 sample of working examples.

Fig.9 shows the texture observation result of AZ31 material. Fig.9 (a) is an observation-by-optical-microscope result of AZ31 start material, Fig.9 (b) is an observation-by-optical-microscope result of 5 - 3 samples of comparative examples, and Fig.9 (c) is an observation-by-optical-microscope result of the comparative example 4-3.

Fig.10 shows the texture observation result by SEM of ZK60 material. Fig.10 (a) is a SEM observation result of the sample which performed solution treatment and aging treatment to 2 - 1 sample of working examples, Fig.10 (b) is a SEM observation result of the sample which performed solution treatment and aging treatment to 3 samples of comparative examples, and Fig.10 (c) shows the SEM observation result to which the black frame part of Fig.10 (a) was expanded.

Also in any of Fig.8 - Fig.10, the direction which tends toward the right from the left of a photograph is a rolling direction (RD), and the direction which goes upwards from the bottom is a rolling face normal line direction (ND).

[0085]

Fig.8 and Fig.9 show that twin crystal is seldom observed with the working-example sample of ZK60 to much twin crystal being observed at the comparative example sample of AZ31.

It is observed in both of the sample which performed solution treatment and aging treatment to the sample which performed solution treatment and aging treatment to 2 - 1 sample of working examples, and 3 samples of comparative examples from Fig.10 that many Zn_2Zr phases deposit. On the other hand, as an arrow showed to Fig.10 (c), many thin rod-like sludge Mg_4Zn_7 (beta1' phase) was accepted, but by the comparative example 3, most Mg_4Zn_7 was not observed in the working example 2-1.

[0086]

- Tensile test

About the sample of the working example 2-1, the comparative example 3, the comparative example 4-3, and the comparative example 6, the tensile test was carried out, after performing solution treatment and aging treatment.

Fig.11 shows the form and the dimension of the specimen used for the tensile test. It cut out from each sample using the wire electric discharge machine (EDM).

The piece of a tensile test was ground by waterproof emery paper #2000, in order to cut out the sample of three directions so that the longitudinal direction (the direction of

tension) may turn into [a rolling direction (the direction of RD), and] the direction of 45 degree, and the rolling width direction (TD direction) from RD, and to remove the influence of an electron discharge method layer.

Initial strain speed of the tensile test was made into $1.67 \times 10^{-3} s^{-1}$, and was examined about each direction in the room temperature atmosphere. The three or more examination was done about each direction, and the maximum of 0.2% proof stress, the minimum and average value, the maximum of a stretch, the minimum, and average value were calculated from this result.

[0087]

Fig.12 is a graph which shows a tensile test result, Fig.12 (a) shows proof stress 0.2%, and Fig.12 (b) shows a stretch.

About proof stress, the working example 2-1 serves as a value (that is, high strength) higher than any of the comparative example 3, the comparative example 4-3, and the comparative example 6 also in which direction 0.2% so that Fig.12 may show.

[0088]

About a stretch value, although the working example 2-1 is the lowest, since about 10% of stretch is still shown in general, it turns out that any sample has the ductility which is satisfactory practically.

[0089]

- Molding examination

The molding examination was carried out about the working example 2-1, the comparative example 3, and the comparative example 6 which have the same thickness 0.9mm in thickness.

About the working example 2-1, the sample which is in the state (namely, state which meant performing a fabricating operation) which was excellent in the moldability and which is not performing aging treatment after solution treatment was used.

[0090]

Fig.13 is a schematic view of a molding testing machine.

The die 12 with which a die radius has space 17 mm in diameter in the central part at 4.0 mm. The specimen (blank) 10 is arranged between the holders 14 which have space 17 mm in diameter at the center, After holding a specimen in prescribed temperature of 100 to 200 degrees C with the heater 16, the punch 18 with a punch diameter of 15 mm was caudad pushed in from the upper part by a part (a part for namely, molding speed/of 10 mm) for 10 mm/.

The punch shoulder radius of the punch 18 was 2.0 mm. 25 mm (therefore, a contraction ratio 1.67 regularity) in diameter, the specimen 10 is 0.9mm in thickness, and it cut out

and produced it from the sample of the working example 2-1, the comparative example 3, and the comparative example 6. About the sample of the working example 2-1, the specimen 10 has been arranged so that the outside of the cup which arises by draw forming may become a side with a quick peripheral speed of asymmetric rolling. Molybdenum disulfide was used as lubricant at the time of a molding examination.

[0091]

Table 5 shows a molding test result. Table 5 shows the sample currently satisfactorily molded with the contraction ratio 1.67 by "O", and molding shows the sample to which the crack of what was made was accepted by "**", and it shows the sample destroyed during molding by "x."

Fig.14 is a photograph to illustrate the sample evaluation result after a molding examination, and Fig.14 (a), An evaluation result shows 2 - 1 sample of working examples after the molding examination which made retention temperature of the specimen 100 degrees C which were "x", and them Fig.14 (b), 3 samples of comparative examples after the molding examination which made retention temperature of the specimen 150 degrees C whose evaluation result was "**" are shown, and Fig.14 (c) shows 2 - 1 sample of working examples after the molding examination which made retention temperature of the specimen 125 degrees C whose evaluation result was "O."

[0092]

[Table 5]

保持温度 （℃）	実施例2－1	比較例3	比較例6
２００		○	○
１７５	○	○○	○
１５０	○	×△	△△
１２５	○△		××
１００	××		

O with :Good **:crack x: -- a fracture

[0093]

The sample which the comparative example 3 cannot already mold at 150 degrees C arose, and the comparative example 6 produced the crack at 150 degrees C, and at 125 degrees C, while it was not already able to mold, at least 125 degrees C of temperature was able to mold the working example 2-1.

Therefore, the working example 2-1 showed the notably outstanding moldability

compared with the comparative example 3 and the comparative example 6.
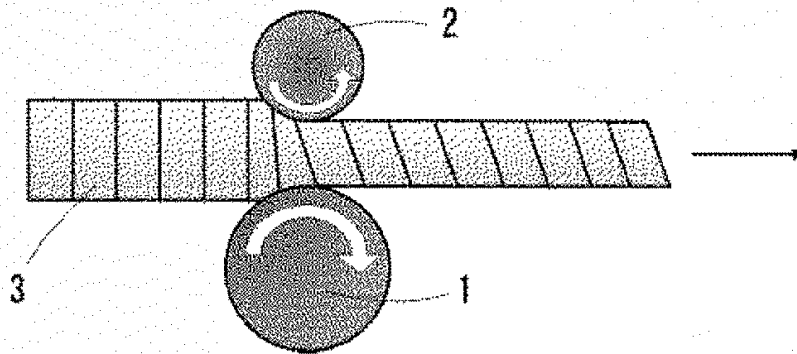
[Explanations of letters or numerals]

[0094]

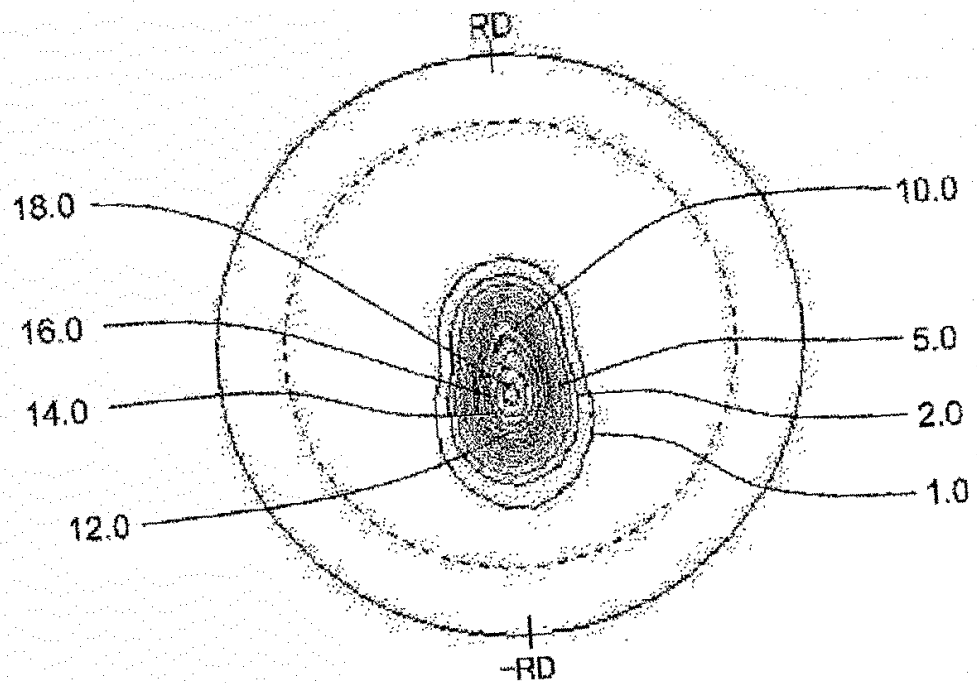1 A high-peripheral-speed rolling roll and 2 [A holder and 16 / A heater and 18 / Punch] A low peripheral-speed rolling roll, 3 magnesium alloy materials, and 10 A specimen (blank) and 12 A die and 14
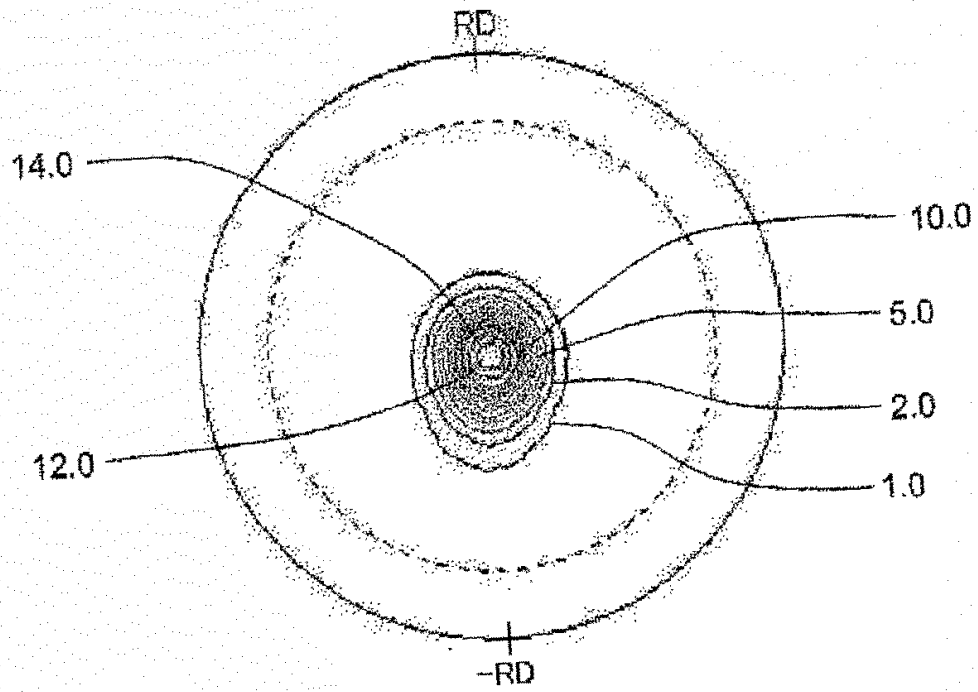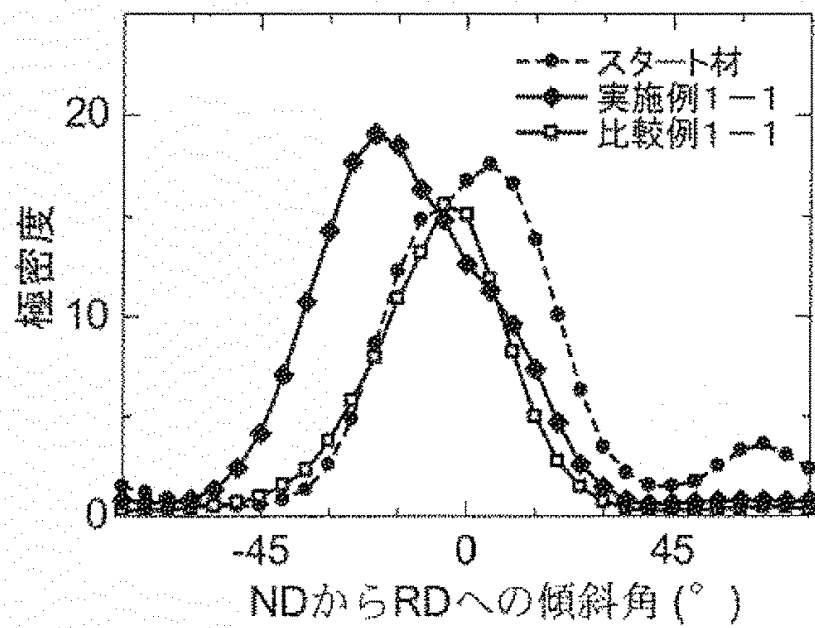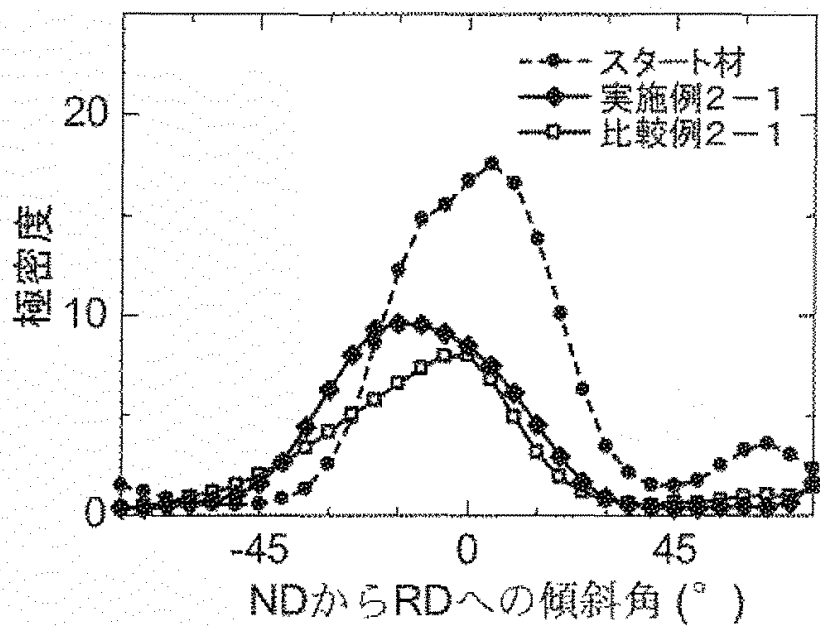
DRAWINGS

[Drawing 1]

[Drawing 2]

RD

18.0

16.0

14.0

12.0

10.0

5.0

2.0

1.0
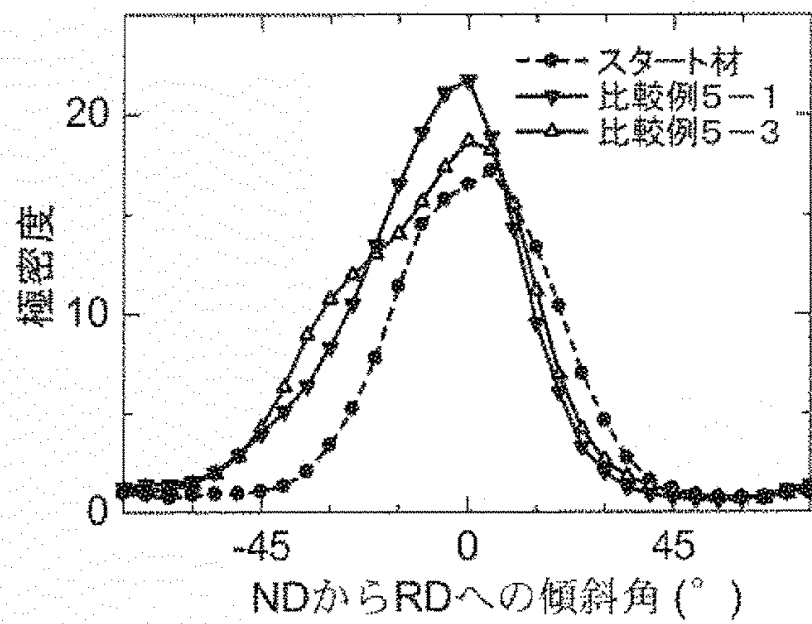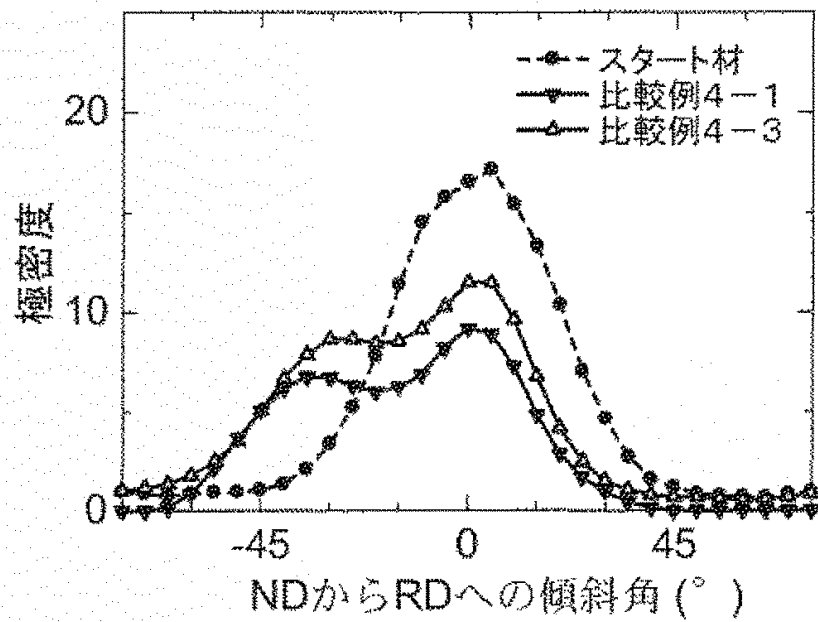
-RD
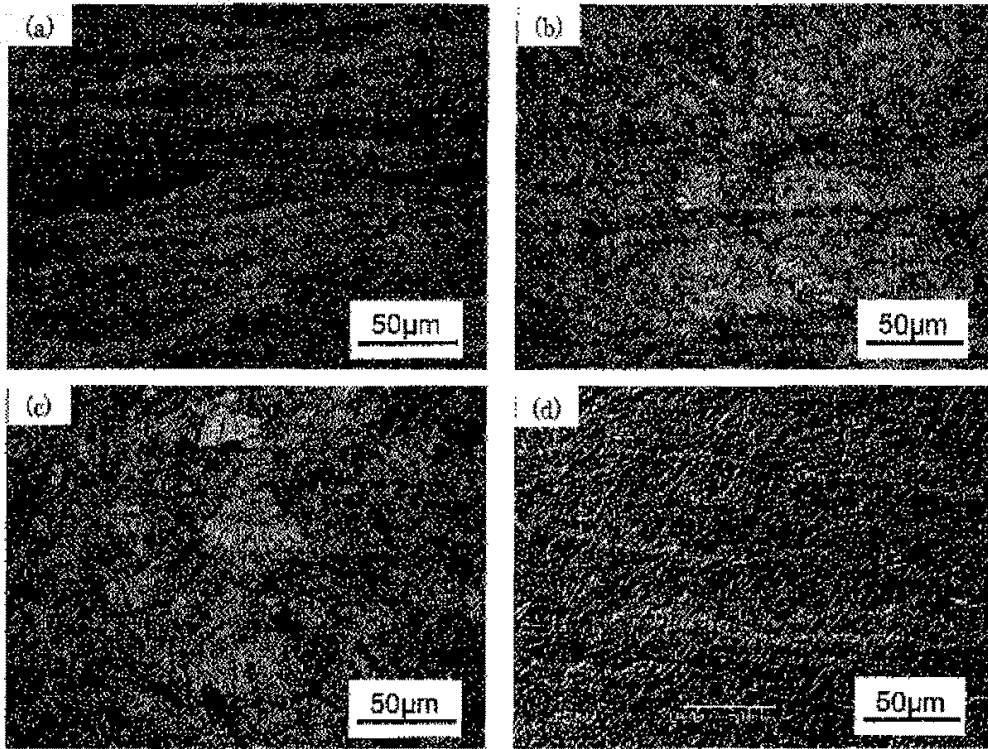
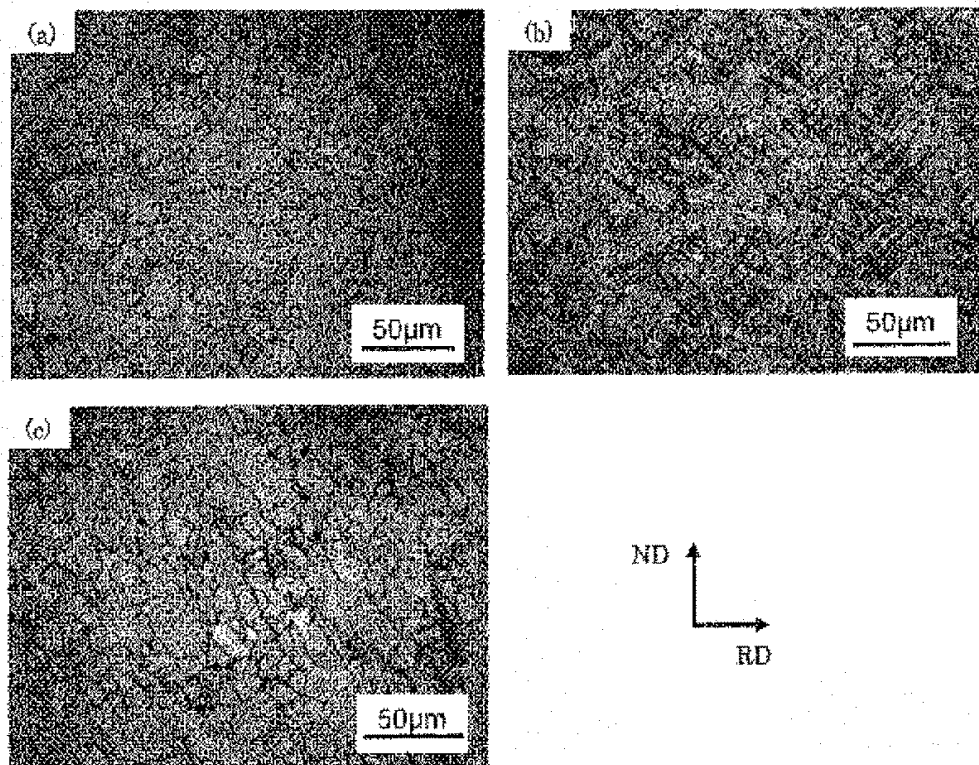[Drawing 3]

RD

14.0

12.0

10.0

5.0

2.0

1.0

−RD

[Drawing 4]

[Drawing 5]

[Drawing 6]

[Drawing 7]

[Drawing 8]

[Drawing 9]

(a) (b) (c)

50μm 50μm 50μm

ND
RD

[Drawing 10]

(a)

(b)

(c)

5μm
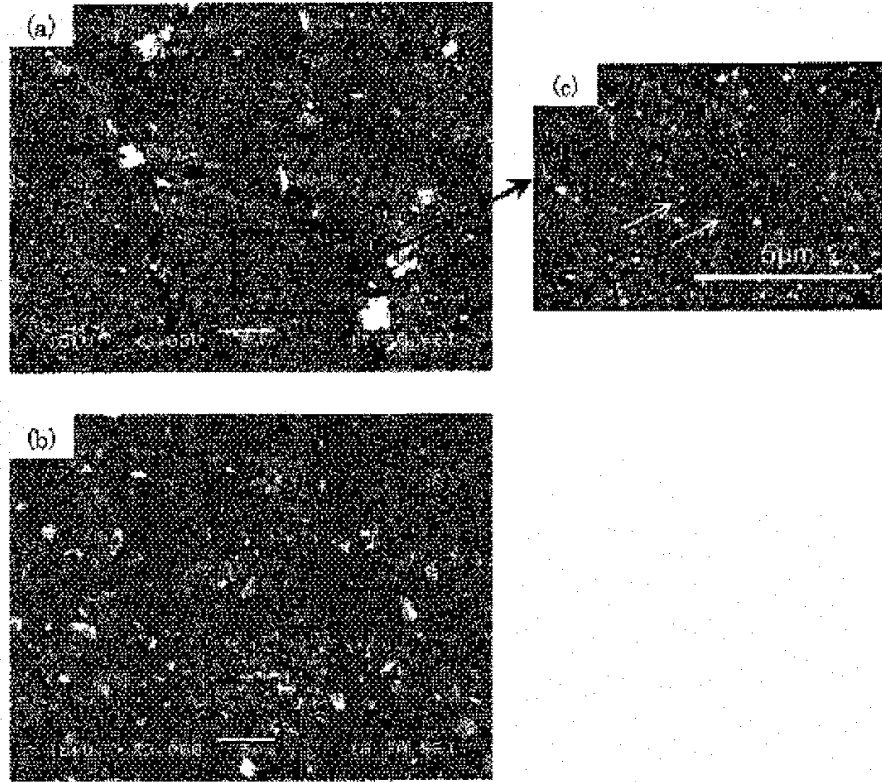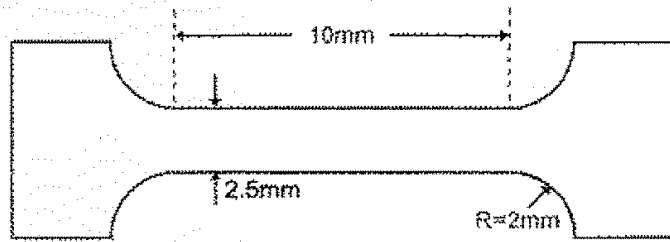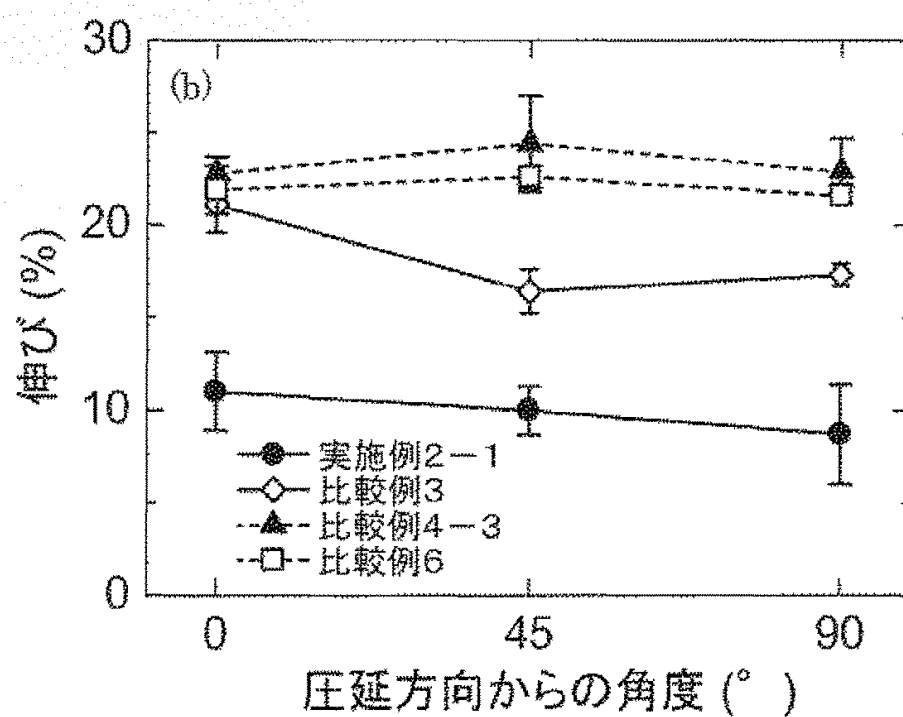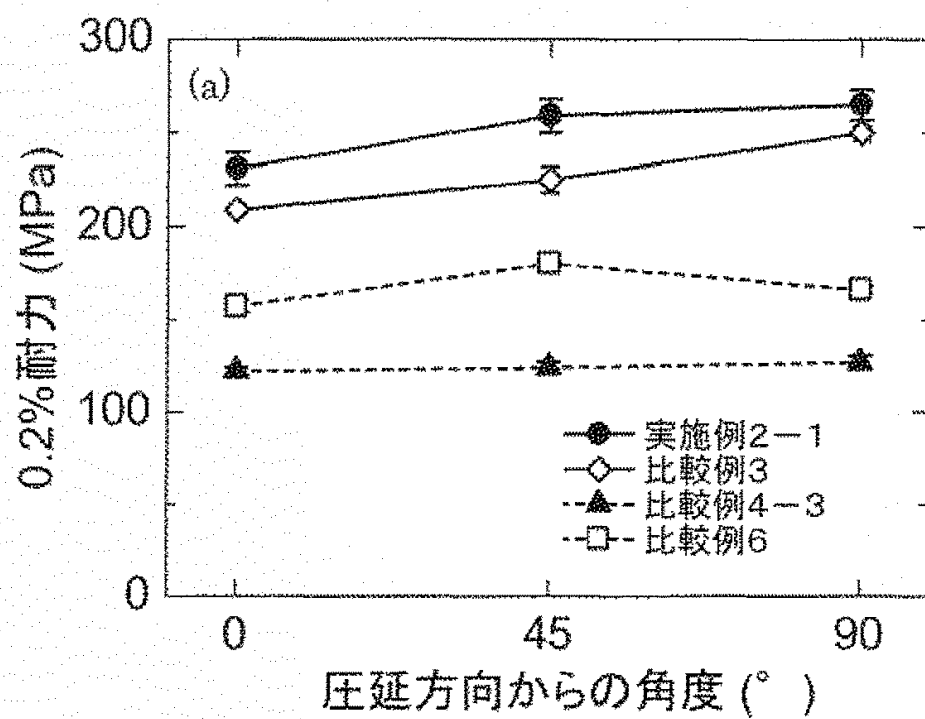
[Drawing 11]

[Drawing 12]

[Drawing 13]

ポンチ荷重

[Drawing 14]

(a)

(b) クラック

(c)

×　　　　　△　　　　　○
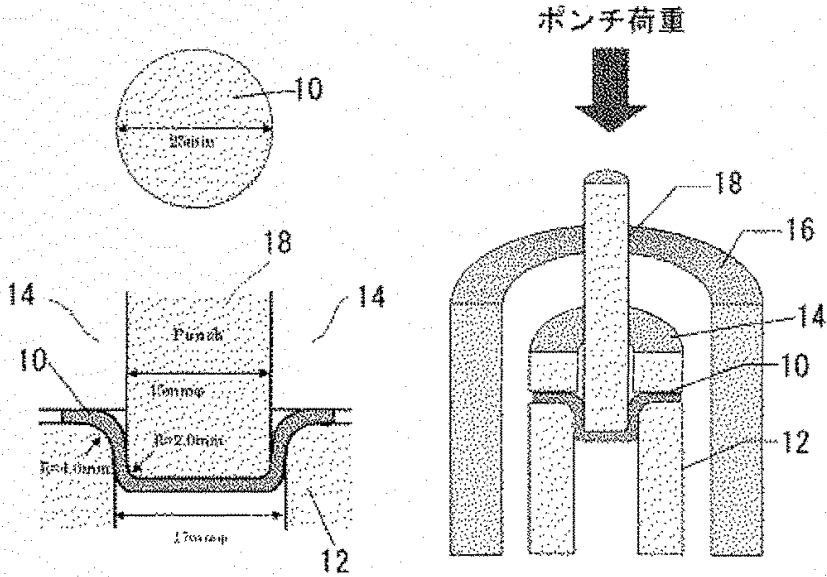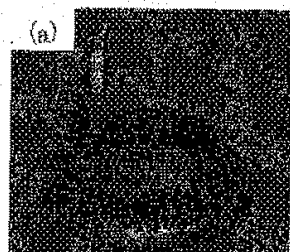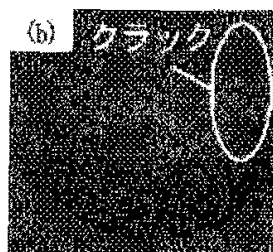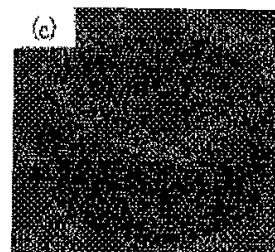
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(54)【発明の名称】マグネシウム合金圧延材およびその製造方法

(57)【要約】

【課題】十分な強度と十分な成形性とを有する析出硬化型マグネシウム合金の圧延材および十分な強度と十分な成形性とを有する析出硬化型マグネシウム合金の圧延材の製造方法を提供する。

【解決手段】50質量%以上のマグネシウムと、3.0～10.0質量%の亜鉛と、0.3～3.0質量%のジルコニウムとを含み、結晶構造が六方最密充填構造（hcp）であるマグネシウム合金圧延材であって、圧延面法線方向から圧延方向への傾斜角がプラスマイナス75°の範囲で測定した、六方最密充填構造のc軸の極密度分布曲線において、極密度のピークが10°以上または－10°以下にあることを特徴とする。

【選択図】図4

【特許請求の範囲】
【請求項1】
　５０質量％以上のマグネシウムと、３．０～１０．０質量％の亜鉛と、０．３～３．０質量％のジルコニウムとを含み、結晶構造が六方最密充填構造（ｈｃｐ）であるマグネシウム合金圧延材であって、
　圧延面法線方向から圧延方向への傾斜角がプラスマイナス７５°の範囲で測定した、六方最密充填構造のｃ軸の極密度分布曲線において、極密度のピークが１０°以上または－１０°以下にあることを特徴とするマグネシウム合金圧延材。
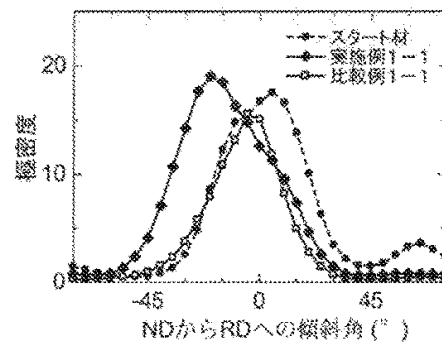【請求項2】
　前記極密度のピークが１５°以上または－１５°以下にあることを特徴とする請求項1に記載のマグネシウム合金圧延材。
【請求項3】
　カルシウムを０．１質量％～１．５質量％含むことを特徴とする請求項1または2に記載のマグネシウム合金圧延材。
【請求項4】
　５０質量％以上のマグネシウムと、３．０～１０．０質量％の亜鉛と、０．３～３．０質量％のジルコニウムとを含み、結晶構造が六方最密充填構造（ｈｃｐ）であるマグネシウム部材を準備する工程と、
　前記マグネシウム合金部材に、圧延温度４４０℃以上、総圧下率５０％以上で異周速圧延を行う工程と、
　を含むことを特徴とする、マグネシウム合金圧延材の製造方法。
【請求項5】
　前記異周速圧延を行った後、３８０℃～５２０℃の間の温度で溶体化処理を行う工程と、
　該溶体化処理を行った後、１２０℃～２５０℃の間の温度で時効処理を行う工程と、
　を更に含むことを特徴とする請求項4に記載のマグネシウム合金圧延材の製造方法。
【請求項6】
　前記溶体化処理と前記時効処理との間にプレス成形を行う工程を更に含むことを特徴とする請求項5に記載のマグネシウム合金圧延材の製造方法。
【請求項7】
　前記マグネシウム部材が、更に、カルシウムを０．１質量％～１．５質量％含むことを特徴とする請求項4～6のいずれか1項に記載のマグネシウム合金圧延材。
【発明の詳細な説明】
【技術分野】
【０００１】
　本発明は、高強度でかつ優れた成形性を有するマグネシウム合金圧延材およびマグネシウム合金圧延材の製造方法に関し、とりわけ高強度でかつ優れた成形性を有する析出強化型マグネシウム合金圧延材およびその製造方法に関する。
【背景技術】
【０００２】
　マグネシウムは実用金属中で最も軽量な金属であり、高い比強度を有し、さらに切削性、制振性、電磁遮蔽性、耐くぼみ性、リサイクル性にも優れている。このためマグネシウムを主成分とするマグネシウム合金が、携帯電話、ノート型パソコンの匡体等の電子機器およびタイヤホイール等の自動車部品を含む幅広い用途で用いられている。
【０００３】
　しかし、マグネシウム合金の圧延材（展伸材）は成形性（加工性）が低いという問題がある。これは、殆どのマグネシウム合金の結晶構造が六方最密充填構造（ｈｃｐ）であること、および圧延加工を行うと底面集合組織を形成することに起因する。底面集合組織とは六方最密充填構造の底面である（０００１）面が圧延面に平行に配向した集合組織、言い換えるとｃ軸（＜０００１＞軸）が圧延面の法線方向に配向した集合組織である。

【０００４】
　一般に成形性（加工性）と強度とは、トレードオフの関係にある。マグネシウム合金においても底面集合組織を減少させることで成形性を向上できるが、通常、底面集合組織が減少すると強度は低下する。
【０００５】
　マグネシウム合金は、例えばＡＺ系合金のような主に固溶強化により強度を得ている固溶強化型合金と、例えばＺＫ系合金のような主に析出強化（または析出硬化）により強度を得ている析出強化型合金の２つに大別できる。
【０００６】
　特許文献１は、ＡＺ系合金に異周速圧延を適用して、強度と成形性を兼ね備えたマグネシウム合金材を得ることを開示している。
　異周速圧延とは、例えば上下に配置されている等の１組のロールにおいて、一方のロールの周速を他方のロールの周速と異ならせ、この２つのロールの間を通過させて圧延を行う圧延方法である。
　特許文献２は、結晶構造が六方最密充填構造（ｈｃｐ）であるマグネシウム合金に異周速圧延を適用して、高い強度を有しかつ成形性に優れたマグネシウム合金圧延材を得ることを開示している。
【先行技術文献】
【特許文献】
【０００７】
【特許文献１】特開２０１０－２０２８９８号公報
【特許文献２】特開２０１１－０５８０５４号公報
【発明の概要】
【発明が解決しようとする課題】
【０００８】
　析出強化型マグネシウム合金（「析出硬化型マグネシウム合金」ともいう）は、析出物により強度を得ることができることから、一般には、固溶強化型マグネシウム合金よりも容易に高い強度を得ることができ、このため、高強度材を得るためには有利な場合が多い。
　しかしながら、特許文献１は、固溶強化型のＡＺ合金を対象にしており、特許文献２は、固溶強化型および析出強化型の両方を含む幅広いマグネシウム合金を対象にしていることから、特許文献１および特許文献２が開示する条件を析出硬化型マグネシウム合金に適用しても、得られた圧延材が所望の強度と所望の成形性とを両立できない場合があった。
【０００９】
　そこで、本願は、十分な強度と十分な成形性とを有する析出硬化型マグネシウム合金の圧延材を提供すること、および十分な強度と十分な成形性とを有する析出硬化型マグネシウム合金の圧延材の製造方法を提供することを目的とする。
【課題を解決するための手段】
【００１０】
　本発明の態様１は、５０質量％以上のマグネシウムと、３．０～１０．０質量％の亜鉛と、０．３～３．０質量％のジルコニウムとを含み、結晶構造が六方最密充填構造（ｈｃｐ）であるマグネシウム合金圧延材であって、圧延面法線方向から圧延方向への傾斜角がプラスマイナス７５°の範囲で測定した、六方最密充填構造のｃ軸の極密度分布曲線において、極密度のピークが１０°以上または－１０°以下にあることを特徴とするマグネシウム合金圧延材である。
【００１１】
　本発明の態様２は、前記極密度のピークが１５°以上または－１５°以下にあることを特徴とする態様１に記載のマグネシウム合金圧延材である。
【００１２】
　本発明の態様３は、カルシウムを０．１質量％～１．５質量％含むことを特徴とする態

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様１または２に記載のマグネシウム合金圧延材である。
【００１３】
　本発明の態様４は、５０質量％以上のマグネシウムと、３．０～１０．０質量％の亜鉛と、０．３～３．０質量％のジルコニウムとを含み、結晶構造が六方最密充填構造（ｈｃ
ｐ）であるマグネシウム部材を準備する工程と、前記マグネシウム合金部材に、圧延温度
４４０℃以上、総圧下率５０％以上で異周速圧延を行う工程と、を含むことを特徴とする
、マグネシウム合金圧延材の製造方法である。
【００１４】
　本発明の態様５は、前記異周速圧延を行った後、３８０℃～５２０℃の間の温度で溶体
化処理を行う工程と、該溶体化処理を行った後、１２０℃～２５０℃の間の温度で時効処
理を行う工程と、を更に含むことを特徴とする態様４に記載のマグネシウム合金圧延材の
製造方法である。
【００１５】
　本発明の態様６は、前記溶体化処理と前記時効処理との間にプレス成形を行う工程を更
に含むことを特徴とする態様５に記載のマグネシウム合金圧延材の製造方法である。
【００１６】
　本発明の態様７は、前記マグネシウム部材が、更に、カルシウムを０．１質量％～１．
５質量％含むことを特徴とする態様４～６のいずれかに記載のマグネシウム合金圧延材。
である。
【発明の効果】
【００１７】
　本願発明では、析出強化型マグネシウム合金を４４０℃以上温度で総圧下率５０％以上
の異周速圧延を行って圧延材を得ることを特徴の１つとする。このようにして得られたマ
グネシウム合金圧延材は、そのｃ軸の極密度分布曲線において、極密度のピークが１０°
以上または－１０°以下となる。
　これにより十分な強度と十分な成形性とを有する析出硬化型マグネシウム合金の圧延材
を提供すること、および十分な強度と十分な成形性とを有する析出硬化型マグネシウム合
金の圧延材の製造方法を提供することが可能となる。
【図面の簡単な説明】
【００１８】
【図１】図１は異周速圧延を説明する模式断面図である。
【図２】図２は実施例１－１サンプルの極点図である。
【図３】図３は比較例１－１サンプルの極点図である。
【図４】ＺＫ６０のスタート材、実施例１－１サンプルおよび比較例１－１サンプルの極
密度分布曲線を示す。
【図５】ＺＫ６０のスタート材、実施例２－１サンプルおよび比較例２－１サンプルの極
密度分布曲線を示す。
【図６】ＡＺ３１のスタート材、比較例５－１サンプルおよび比較例５－３サンプルの極
密度分布曲線を示す。
【図７】図７はＡＺ３１のスタート材、比較例４－１サンプルおよび比較例４－３サンプ
ルの極密度分布曲線を示す。
【図８】ＺＫ６０材の組織観察結果を示す。図８（ａ）はＺＫ６０スタート材の光学顕微
鏡観察結果であり、図８（ｂ）は実施例１－１サンプルの光学顕微鏡観察結果であり、図
８（ｃ）は実施例２－１サンプルの光学顕微鏡観察結果であり、図８（ｄ）は実施例２－
１サンプルのＳＥＭ観察結果である。
【図９】ＡＺ３１材の組織観察結果を示す。図９（ａ）は、ＡＺ３１スタート材の光学顕
微鏡観察結果であり、図９（ｂ）は比較例５－３サンプルの光学顕微鏡観察結果であり、
図９（ｃ）は比較例４－３の光学顕微鏡観察結果である。
【図１０】ＺＫ６０材のＳＥＭによる組織観察結果を示す。図１０（ａ）は実施例２－１
サンプルに溶体化処理と時効処理を施したサンプルのＳＥＭ観察結果であり、図１０（ｂ

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）は比較例３サンプルに溶体化処理と時効処理を施したサンプルのＳＥＭ観察結果であり、図１０（ｃ）は図１０（ａ）の黒枠部を拡大したＳＥＭ観察結果を示す。
【図１１】引張り試験に用いた試験片の形状および寸法を示す。
【図１２】引張り試験結果を示すグラフであり、図１２（ａ）は０．２％耐力を示し、図１２（ｂ）が伸びを示す。
【図１３】成形試験機の概略図である。
【図１４】成形試験後のサンプル評価結果を例示する写真であり、図１４（ａ）は、評価結果が「×」であった、試験片の保持温度を１００℃とした成形試験後の実施例２－１サンプルを示し、図１４（ｂ）は、評価結果が「△」であった、試験片の保持温度を１５０℃とした成形試験後の比較例３サンプルを示し、図１４（ｃ）は、評価結果が「○」であった、試験片の保持温度を１２５℃とした成形試験後の実施例２－１サンプルを示す。
【発明を実施するための形態】
【００１９】
　　以下、図面に基づいて本発明の実施形態を詳細に説明する。なお、以下の説明では、必要に応じて特定の方向や位置を示す用語（例えば、「上」、「下」、「右」、「左」及びそれらの用語を含む別の用語）を用いるが、それらの用語の使用は図面を参照した発明の理解を容易にするためであって、それらの用語の意味によって本発明の技術的範囲が限定されるものではない。
【００２０】
　　本願発明者は、詳細を後述するように、析出強化型マグネシウム合金を４４０℃以上の温度で総圧下率５０％以上の異周速圧延を行うことにより、六方最密充填構造を有する得られた圧延材のｃ軸（＜０００１＞軸）の配向を示す、極密度分布曲線のピークが、０°から１０°以上シフトし（すなわち、ピークの位置が１０°以上または－１０°以下であり）、好ましくは、０°から１５°以上シフトする（すなわち、ピークの位置が１５°以上または－１５°以下である）ことを見出した。
【００２１】
　　このことは、ｃ軸の配向が圧延面の法線方向から圧延方向または圧延逆方向に１０°以上、好ましくは１５°以上傾いていることを意味する。
　　そして、本願発明に係る析出強化型マグネシウム合金おいては、極密度分布曲線のピークが、０°から１０°以上シフトした（すなわち、ピークの位置が１０°以上または－１０°以下である）状態は、溶体化処理および時効処理を行っても維持される。
【００２２】
　　従って、異周速圧延を行った後、溶体化処理を行うことにより、より優れた成形性を実現できる。そして、所望の形状に加工を行った後に時効処理を行うことにより、析出物を析出させ、材料強度を十分に高くすることができる。上述のように、極密度分布曲線のピークが、０°から１０°以上シフトしている本願発明のマグネシウム合金圧延材は、時効処理により十分に高い強度に到達しかつ必要な延性（および靭性）を確保することができる。
　　すなわち、本願発明に係るマグネシウム合金圧延材は、十分な強度と十分な成形性とを両立することができる。
【００２３】
　　以下に本願発明の詳細を説明するが、最初に本発明を理解するのに不可欠な極密度分布曲線について説明する。
【００２４】
１．極密度分布曲線
　　極密度分布曲線の求め方を説明する。
　　まず、Ｘ線回折による、集合組織等の結晶配向の評価法として最も一般的なＳｃｈｕｌｚの反射法を用いて（０００２）面の極点図を求める。
　　反射強度分布の概要が明確に把握できるように、極点図の測定の際のα角は、極点図の外周円から１５°～９０°の範囲とするのが望ましい。また測定はα角、β角とも例えば

5°毎のように3〜10°毎に行うのが好ましい。10°より大きいと測定精度が低下する恐れがあり、3°より小さいと測定時間を必要以上に要するからである。

【0025】

　図2は、詳細を後述する実施例1-1サンプルの極点図であり、図3は、詳細を後述する比較例1-1サンプルの極点図である。

　これらは圧延材の極点図として一般的なステレオ投影の表示方法を用いている。図中に示すように、円形のステレオ投影面の最上部がRD（圧延方向）を示し、最下部が-RD（圧延逆方向）示す。図中に記載していないが、ND（圧延面法線方向）は投影面の中心となる。そして図中に等高線状に現れているのが様々なα角とβ角に対応する方向で観測されたX線の（0002）面の極密度であり、該当する位置での（0002）回折強度を無配向の粉末試料の（0002）回折強度で除した値である。従って、極密度1の値はランダム方位の極密度を示す。

【0026】

　なお、本明細書において、RDと-RDは、圧延の入口側を-RD（圧延逆方向）、圧延の出口側をRD（圧延方向）としている。また、異周速圧延を行ったサンプルについては周速の早いロール側の圧延面と周速が遅いロール側の圧延面ではせん断応力の向きが反対になるため、互いの面から得た極点図は、裏返して上下を入れ替えた関係となる。そこで、本明細書においては周速の速いロール側の圧延面（これを研磨した面）から極点図を得るものとする。

【0027】

　ただし、嚙え間違ってあるいはどちらか判らずに周速の遅いロール側の圧延面から極点図を得たとしても、上述の対応関係にあることから、これから説明する極密度分布曲線を得てその特性値であるピークのシフト量（中心値である0°からのずれ）については同等の結果を得ることができる。

【0028】

　次に得られた極点図から極密度分布曲線を得る。極密度分布曲線の測定結果を例示する。図4に示す実施例1-1サンプルの極密度分布曲線は上述の図2に示す極点図のデータを用いて得たものであり、図4中の比較例1-1サンプルの極密度分布曲線は上述の図3に示す極点図のデータを用いて得たものである。

【0029】

　極密度分布曲線を示すグラフの横軸は、ND（圧延面の法線）からの傾斜角であり、極点図（ステレオ面）において、-RDからND（ステレオ面の中心）を経てRDに至る直線上の位置に対応している。そして、傾斜角は-RD側を負で表し、RD側を正で示す。

　一方、極密度分布曲線を示すグラフの縦軸は、極点図の該当する位置の極密度である。

【0030】

　このようにして求めた極密度分布は、圧延材の幅方向に垂直であり、かつNDに対する傾斜角がθであるc軸の極密度を示している。

【0031】

　極密度分布曲線は、その全体像を明瞭にするために、極点図測定範囲の-75°〜+75°（すなわち、ND方向からRD方向に±75°）を表示することが好ましい。そして、これは上述の極点図の測定においてα角を15°〜90°とすることで実現できる。

【0032】

　底面集合組織が発達すると傾斜角が0°の付近に極密度の鋭いピークが観察される。一方、底面集合組織機が減少すると、その減少の形態に応じて、傾斜角が0°から離れた位置へのピークのシフト、ピークのブロードニングおよび／またはダブルピークの出現等が起こる。

　従って、極密度分布曲線を得ることにより、底面集合組織の多少等を定量的に把握することが可能となる。

【0033】

２．異周速圧延

　以下に本発明の異周速圧延について、説明する

　図１は、異周速圧延を説明する模式断面図である。ロール１とロール２とからなる一組
の圧延ロールが配置され、その間をマグネシウム合金材３が通過し圧延される。図１に示
す実施形態では、ロール１の直径をロール２の直径よりも大きくし、ロール１とロール２
とを同じ回転速度（角速度）で回転させることにより、ロール１の周速をロール２の周速
より速くしている。ロール１および２はそれぞれ、図中に白抜き矢印で示す方向に回転す
る。

【００３４】
　ロール１の周速をロール２の周速より速くする方法は、もちろんこれに限定されるもの
でなく、例えばロール１とロール２を同じ直径にしてロール１の回転速度を高くする等の
従来から知られている任意の方法を用いることができる。

【００３５】
　異周速圧延を行うことにより圧延材にせん断応力を作用させることができる。より詳細
には周速の速いロール１側では図中に黒矢印で示したマグネシウム合金材３の圧延方向（
ＲＤ）、すなわち図１の右方向にせん断応力を受ける。一方、周速の遅いロール２側では
、圧延方向と１８０°反対方向の圧延逆方向（－ＲＤ）、すなわち図１の左方向にせん断
応力を受ける。

【００３６】
　マグネシウム合金材３中の縦線はこのせん断応力による圧延材への影響を模式的に示す
ものである。異周速圧延の前にマグネシウム合金材に仮想的に引いた垂直な縦線は、異周
速圧延により上述のようにせん断応力が付加されることにより、ロール１側がＲＤ方向に
ロール２側が－ＲＤ方向にシフトした斜めの線となる。

【００３７】
　本発明に係る異周速圧延では、圧延温度４４０℃以上、かつ総圧下率を５０％以上とす
ることを特徴とする。これにより、ｃ軸の極密度分布曲線において、極密度のピークを０
°から確実に１０°以上シフトさせることが可能となる。
　好ましくは、圧延温度は４７０℃以上である。これにより、より高い強度でより優れた
成形性を得ることができる。
　また、圧延温度は好ましくは５５０℃以下である。圧延温度は５５０℃を超えると固相
線を超え、部分溶融する場合があるからである。

【００３８】
　なお、加工中の材料の温度、とりわけ圧延中のマグネシウム合金材の温度を測定するこ
とは実際上極めて困難なことから、本明細書でいう圧延温度とは、圧延工程において圧延
加工直前に加熱し、引き続いて（意図的に遅延させることなく）圧延を行う際の前記加熱
時の材料の加熱温度（または到達温度）を意味する。

【００３９】
　また、異周速圧延の総圧下率とは、異周速圧延を１パスのみ行った場合は、その１パス
の圧下率を意味し、異周速圧延を複数パス行った場合は、複数パス全体の圧下率（すなわ
ち、当該複数パスの異周速圧延を行う前の板厚と当該複数パスの異周速圧延を行った後の
板厚から求める圧下率）である。圧延加工性と導入されるせん断ひずみ量を考慮すると、
好ましくは、１パスあたりの圧下率を５～３０％として、複数パスにより５０％以上の総
圧下率を確保するのが好ましい。

【００４０】
　このような複数パスの圧延は、１パス圧延する毎に再度所定の圧延温度まで加熱して次
のパスを行ってもよい。また所定の圧延温度まで加熱したのち複数パスの連続圧延を行っ
てもよい。

【００４１】
　さらに、等周速圧延と異周速圧延とを連続圧延により実施してもよい。この場合、異周
速圧延の総圧下率とは異周速圧延による板厚の変化から求める圧下率を意味する。

【００４２】

　また、異周速圧延を行う材料は、鋳造スラブ、通常の圧延材（等周速圧延材）、ダイカスト等の押し出し材等の各種の材料を用いることができる。歪みを除去するために、異周速圧延を行う前に例えば３００℃～４５０℃の範囲の温度で１０分間以上保持するアニーリングを適宜行ってよい。

【００４３】

　なお、例えばＡＺ３１合金のような固溶強化型のマグネシウム合金材を４４０℃以上の圧延温度でかつ総圧下率５０％以上の圧延条件で異周速圧延を行っても多くの場合、得られた圧延材の極密度分布曲線のピークのシフトは１０°未満である。これはダブルピークの場合に片方のピークが１０°未満であることを述べたものであり、もう一方のピークの位置を限定するものではない。

【００４４】

　本願発明に係る析出硬化型マグネシウム合金を圧延温度４４０℃以上、かつ総圧下率を５０％以上で異周速圧延することにより、得られた圧延材の極密度分布曲線のピークが、１０°以上シフトする理由、およびこのように０°から１０°以上シフトしたピークを有する本願発明に係る圧延材が溶体化後に優れた成形性を有し、かつ時効処理後に十分な強度を有する理由については、まだ不明な点も多いが、発明者の考えるメカニズムは以下の通りである。しかし、この予想されるメカニズムは、本発明の技術的範囲を制限することを意図したものではない。

【００４５】

　ＡＺ３１のような固溶強化型マグネシウム合金の場合、４４０℃以上のような高温で異周速圧延すると、喩え、圧延の総圧下率が低くても得られた圧延材の極密度分布曲線のピークが第１ピーク（メインピーク）と第２ピーク（サブピーク。通常、メインピークより高さの低いピーク）の２つのピークが現れる。そして、第２のピークは１０°以上シフトすることが多い（例えば、詳細を後述する図７の比較例４－３等）がしかし、メインピークは通常１０°以上シフトすることはない。

　第２ピークが１０°以上シフトするのは、異周速圧延中に方位変化の大きな双晶変形が起こりやすいためと考えられる。そして、この双晶変形は低い総圧下率で起こるために、元の底面集合組織（第１ピーク）から容易に第２ピークを形成する。

　従ってｃ軸が傾くが、メインピークが１０°以上シフトするということはない。

　これに対してＺＫ６０合金等の析出強化型マグネシウム合金の場合、高温で異周速圧延を行っても双晶変形は起こりにくい（従って、得られた圧延材の極密度分布曲線のピークが２つに分離することもない）。この結果、底面すべりに加えて底面すべり以外のすべり系、特にｃ＋ａすべりが活動するために、圧下率の増加とともに徐々にｃ軸が傾くと考えられる。そして、総圧下率を５０％以上とすることで、ピークが１０°以上シフトすると思われる。

　ｈｃｐ構造を有するマグネシウム合金は、通常、溶体化処理中に生じる再結晶によっても、ｃ軸の傾きがそれほど変化しないため、異周速圧延により、ピークが大きくシフトした（ｃ軸が大きく傾いた）集合組織を有する本願発明に係る圧延材は、溶体化後のプレス成形の際でも底面すべりが活動しやすく、その結果として優れた成形性を有すると考えられる。

【００４６】

　また、後述する実施例で詳細を示すように、圧延温度４４０℃以上で異周速圧延を行った本願発明に係る圧延材は、圧延温度３００℃程度の通常の等周速圧延を行った圧延材と比べて溶体化処理と時効処理を行った後の材料強度が高くなっている。

　これは、圧延温度が高いために圧延中の析出が起こりにくく、圧延後には添加元素をより多く固溶した状態となり、この状態が溶体化処理を行っても維持されるため、溶体化処理後でも添加元素の固溶量が多く、その後の時効処理によって析出する微細析出物の量が多くなるためと考えられる。

　以上のような理由で、本願発明においては、析出強化型マグネシウム合金を４４０℃以上で異周速圧延することで、溶体化状態で成形性に優れ、かつ時効状態で高い強度を有す

るマグネシウム合金板材が得られると考えられる。

【００４７】

　異周速圧延の周速比（１組のロールのうち遅い方の周速を１としたときの速い方の周速の比）は、好ましくは１．４～２．０である。周速が１．４以上だと圧延時により大きなせん断応力が発生するため、より容易にｃ軸を圧延方向または圧延方向と反対側に傾斜させる（すなわち、極密度分布曲線のピークがより容易に０°からシフトする）ことができるからである。一方、周速比が２．０を超えると、材料とロールの間の滑りが生じやすくなり安定した圧延を行うことが難しくなるとともに、材料の表面性状が著しく悪くなる場合があるからである。

【００４８】

　また、圧延後の冷却は、空冷であってもよく、また水冷等の急速冷却を行ってもよい。好ましくは、急速冷却を行う。室温に冷却されるまでの間に析出物が析出するのを抑制できるからである。

【００４９】

３、溶体化処理

　上述の異周速圧延を行った、析出強化型マグネシウム合金の圧延材は、続いて溶体化処理を行うことが好ましい。溶体化処理は、圧延工程までに析出した析出物をマトリクスに固溶させることを主な目的として実施する。

　溶体化処理は、好ましくは、３８０℃～５２０℃の間の温度で実施する。溶体化温度が３８０℃より低いと、析出物がマトリクスに十分に固溶せず析出物が多く残存する場合があり、５２０℃を越えると結晶粒が粗大化する場合があるからである。

【００５０】

　また、溶体化の保持時間（所定の溶体化温度に到達後保持する時間）は、好ましくは１時間～４８時間である。これは、溶質原子を十分に固溶させるために、溶質原子の拡散速度を考慮して溶体化温度に応じて、拡散のための時間が必要であるからである。また、後の成形のために、溶体化処理後の組織が等軸粒の再結晶組織であることが好ましい。

【００５１】

　溶体化処理後は、例えば水中に焼き入れる等により急冷することが好ましい。冷却中に析出物が析出するのを防止できるからである。

【００５２】

　上述のように、溶体化処理を行っても、上述の異周速圧延により得られた、極密度分布曲線のピーク位置が０°より１０°以上シフトしている（すなわち、ピークの位置が１０°以上であるか、または－１０°以下である）状態が維持される。

【００５３】

　すなわち、溶体化後の状態は、析出物が少なく、かつ底面集合組織が低減した状態であることから、溶体化を行わない場合と比べ、成形性により優れている。

【００５４】

４．成形

　上述の異周速圧延を行った後（好ましくは、更に上述の溶体化処理を行った後）に、所望の形状に成形する。

　成形は、任意の成形方法（または塑性変形方法）を用いてよい。このような成形方法として、プレス成形（絞り成形、曲げ成形および張り出し成形を含む）を例示できる。

　成形は、割れが生じなければ冷間で行ってもよいし、温間または熱間で行ってもよい。

【００５５】

５．時効処理

　上述の成形を行った後、時効処理を行って析出物を析出させることにより、材料強度を増加させる。

　時効処理は、後述する合金組成によるが、好ましくは１２０℃～２５０℃の間の温度（時効温度）、より好ましくは１５０℃～２１０℃の間の温度で行う。時効温度が低すぎると十分な量の析出物を得ることができない場合があり、時効温度が高過ぎると析出物が粗

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大化しやすく高い強度が得られない場合があるからである。
【００５６】
　また、上述の時効温度で保持する保持時間は、好ましくは２４時間～２００時間であり
、より好ましくは４８時間～１５０時間である。時効時間が短いと十分な量の析出物を得
ることができない場合があり、時効時間が長いと析出物が粗大化し高い強度が得られない
場合があるからである。
【００５７】
　時効処理により析出する析出物は、合金組成に依ることから、合金組成の項目で詳述す
る。
【００５８】
　なお、本願発明では、上述の異周速圧延を行うことにより、極密度のピークが１０°以
上または－１０°以下にあることを特徴とするマグネシウム合金圧延材を得ている。
　そして、極密度のピークが１０°以上または－１０°以下にある状態は、溶体化処理後
、すなわち成形前まで維持されている。さらに、溶体化処理後に成形を行わなければ、こ
の状態は時効処理後も維持される。
【００５９】
　従って、本願発明に係るマグネシウム合金圧延材とは、異周速圧延を行った直後の圧延
材はもとより、溶体化処理された圧延材、成形された圧延材および時効処理された圧延材
を含む概念である。
【００６０】
６．合金組成
　以上に説明した本発明にかかるマグネシウム合金圧延材に用いる析出強化型マグネシウ
ム合金は、マグネシウム（Ｍｇ）を主成分とし（すなわち、マグネシウムを５０質量％以
上含有し）、３．０～１０．０質量％の亜鉛（Ｚｎ）と、０．３～３．０質量％のジルコ
ニウム（Ｚｒ）とを含むマグネシウム合金である。
【００６１】
　本発明にかかるマグネシウム合金圧延材に用いるマグネシウム合金は、このような組成
を有し、かつ結晶構造が六方最密充填構造（ｈｃｐ）であることを特徴とする。
　そして、このような組成と結晶構造を有するマグネシウム合金に上述の異周速圧延を行
うことで、圧延面法線方向から圧延方向への傾斜角がプラスマイナス７５°の範囲で測定
した、ｃ軸の極密度分布曲線において、極密度のピークが１０°以上または－１０°以下
とすることができる。
【００６２】
　亜鉛は、強度、耐食性、鋳造性の向上という効果を有し、３．０質量％より少ないとこ
れらの効果がない場合があり、１０．０質量％より多いとＭｇ－Ｚｎ系金属間化合物が多
量に存在する場合がある。
　上記の効果をより確実に得るために、より好ましくは、亜鉛の量は４．０～７．０質量
％であり、更により好ましくは４．８～６．２質量％である。
　なお、本項目「６．合金組成」に示した組成は材料全体の平均組成であって、局所的な
組成を意味するものではない。
【００６３】
　ジルコニウムは、結晶粒微細化と熱間加工性向上という効果を有し、０．３質量％より
少ないとこれらの効果が十分でない場合があり、３．０質量％より多いとＺｎ－Ｚｒ系金
属間化合物やＺｒ固溶体が過多となる場合がある。なお、上記の効果をより確実に得るた
めに、より好ましくは、ジルコニウムの量は０．４～２．０質量％であり、更により好ま
しくは０．５～１．５質量％である。
【００６４】
　なお、このような組成を有する本願発明に係るマグネシウム合金に時効処理を行った場
合の析出物として、例えば、Mg_4Zn_7（$\beta_1{}'$相）およびZn_2Zrを例示できる。
【００６５】

　また、このような組成を有するマグネシウム合金として、例えば、３．０～１０．０質量％の亜鉛と、０．３～３．０質量％のジルコニウムとを含み、残部がマグネシウムおよび合計で１．０質量％以下のその他の元素（例えば、不純物）よりなるマグネシウム合金を挙げることができる。

【００６６】
　しかし、本願発明に用いるマグネシウム合金は、此に限定されるものではない。５０質量％以上のマグネシウム（Ｍｇ）と、３．０～１０．０質量％の亜鉛（Ｚｎ）と、０．３～３．０質量％のジルコニウム（Ｚｒ）を含有し、結晶構造が六方最密充填構造（ｈｃｐ）であれば、他の任意の元素を更に含んでいても、異周速圧延により極密度のピークが１０°以上または－１０°以下とすることで、優れた成形性と高い強度とを両立し得る。

【００６７】
　このような他の任意の元素および当該元素の効果的な添加量として、以下を例示できる。
・Ｃａ
　Ｃａは、防燃性の効果を有する。この効果は、添加量を０．１質量％～１．５質量％とすることで確実に得ることができる。

【００６８】
　また、本願発明に係るマグネシウム合金の各種の特性の改善のためにＣａ以外の任意の元素を含んでよい。

【実施例】
【００６９】
１．実施例１
・スタート材
　表１は、以下に詳述する実施例および比較例サンプルを得るのに用いた２つの合金、ＺＫ６０Ａ（以下、「ＺＫ６０」という）およびＡＺ３１Ｂ（以下、「ＡＺ３１」という）のスタート材の組成を示す。
　スタート材として、厚さ３ｍｍの市販の圧延材（等周速圧延材）を用いた。

【００７０】
【表１】

（質量％）

	Ａｌ	Ｚｎ	Ｚｒ	Ｍｎ	Ｆｅ	Ｓｉ	Ｃｕ	他	Ｍｇ
ＺＫ６０Ａ		4.8～6.2 標準値 5.5	>0.45 標準値 0.6					<0.3	残部
ＡＺ３１Ｂ	2.70	1.10		0.42	0.003	0.02	<0.01	<0.3	残部

【００７１】
・圧延
　上記のスタート材を用いて圧延材を行った。それぞれのサンプルの圧延条件を表２に示す。
　異周速圧延は、図１に示す圧延ロールを用いて行った。ロール１の直径は１４４ｍｍであり、ロール２の直径は９６ｍｍである。ロール１とロール２とを回転させることにより周速比１．５の異周速圧延を行った。
　１パスの圧下率は約１０％であり、複数パスの異周速圧延を行い表２に示す総圧下率（トータル圧下率）を得た。

【００７２】
　等周速圧延は、１組の直径１５０ｍｍのロールを用いて行った。１パスの圧下率は約１０％であり、複数パスの等周速圧延を行い表２に示す７０％の総圧下率を得た。

【００７３】

【表2】

サンプル	スタート材 （合金種別）	圧延種別	圧延温度（℃）	トータル圧 下率（％）
実施例1－1	ＺＫ６０	異周速圧延	４５０	７０
実施例1－2	ＺＫ６０	異周速圧延	４５０	５０
比較例1－1	ＺＫ６０	異周速圧延	４５０	３０
比較例1－2	ＺＫ６０	異周速圧延	４５０	２０
実施例2－1	ＺＫ６０	異周速圧延	５００	７０
実施例2－2	ＺＫ６０	異周速圧延	５００	５０
比較例2－1	ＺＫ６０	異周速圧延	５００	３０
比較例2－2	ＺＫ６０	異周速圧延	５００	２０
比較例3	ＺＫ６０	等周速圧延	３００	７０
比較例4－1	ＡＺ３１	異周速圧延	４５０	７０
比較例4－2	ＡＺ３１	異周速圧延	４５０	５０
比較例4－3	ＡＺ３１	異周速圧延	４５０	３０
比較例5－1	ＡＺ３１	異周速圧延	３００	７０
比較例5－2	ＡＺ３１	異周速圧延	３００	５０
比較例5－3	ＡＺ３１	異周速圧延	３００	３０
比較例5－4	ＡＺ３１	異周速圧延	３００	２０
比較例6	ＡＺ３１	等周速圧延	３００	７０

【００７４】
・熱処理
　合金種別がＺＫ６０であるサンプル（実施例1－1、実施例1－2、比較例1－1、比較例1－2、実施例2－1、実施例2－2、比較例2－1、比較例2－2および比較例3）は、４００℃で２４時間の溶体化処理を行った後、１８０℃で９６時間の時効処理を行った。
　一方、合金種別がＡＺ３１であるサンプル（比較例4－1～4－3、比較例5－1～5－4おおび比較例6）は、３００℃で３０分間の焼鈍（アニーリング）を行った。
【００７５】
　・極密度分布曲線の測定
　スタート材および圧延後のサンプルについて、以下に示す方法により極密度分布曲線も求めた。
【００７６】
　まず、それぞれのサンプルの（０００１）極点図をＳｃｈｕｌｚの反射法により求めた。それぞれのサンプルから２５ｍｍ×２５ｍｍの試料を切り出し、この試料を耐水エメリー紙で板厚を半分程度まで削った後に＃２０００で仕上げ研磨した試料を用いて測定した。異周速圧延を行ったサンプルについては、周速の速いロール側の面を削って研磨し測定面とした。
【００７７】
　α＝１５°～９０°の範囲で極点図を作成した。回折角度は理論角付近をスキャンさせ、半値幅中点法により求めた角度を使用した。バックグラウンドの測定角度は回折角度±２°を基本とするが、他の回折線と部分的に重なるために（１０－１０）の回折角度－２°、（１０－１１）の回折角度＋２°とした。得られた回折強度にバックグランド補正、および純Ｍｇ粉末を用いたランダム試料による強度補正を行い、極点図を得た。測定に関する諸条件を表3に示す。
【００７８】

【表3】

Ｓｃｈｕｌｚの反射法測定条件

X線源	ＣｕＫα線
シュルツスリット	1mm
発散スリット	1°
α走査範囲	15°〜90°
β走査範囲	0°〜360°
αステップ幅	5°
βステップ幅	5°
γ振動幅	5mm

【００７９】
　得られた（０００１）極点図をもとに、－ＲＤからＮＤを経てＲＤに至る、傾斜角±７５°の範囲の極密度分布曲線を作成した。
　図２および３に測定した極点図を例示する。図２は実施例１－１サンプルの極点図であり、図３は比較例１－１サンプルの極点図である。
【００８０】
　図４〜図７に極密度分布曲線を例示する。図４はＺＫ６０のスタート材、実施例１－１サンプルおよび比較例１－１サンプルの極密度分布曲線を示す。図５はＺＫ６０のスタート材、実施例２－１サンプルおよび比較例２－１サンプルの極密度分布曲線を示す。図６はＡＺ３１のスタート材、比較例５－１サンプルおよび比較例５－３サンプルの極密度分布曲線を示す。図７はＡＺ３１のスタート材、比較例４－１サンプルおよび比較例４－３サンプルの極密度分布曲線を示す。
【００８１】
　このようにそれぞれのサンプルの極密度曲線を求め、そのピークの位置を表４に示す。なお、図７の比較例４－１のように、ピークが２つ認められる場合は、高さの高い方のピークの位置を当該サンプルのピーク位置とした。
【００８２】

【表４】

サンプル	状態	ピーク位置（°）
ＺＫ６０スタート材	スタート材	5
ＡＺ３１スタート材	スタート材	5
実施例１－１	圧延後	－２０
実施例１－２	圧延後	－１０
比較例１－１	圧延後	－５
比較例１－２	圧延後	０
実施例２－１	圧延後	－１５
実施例２－２	圧延後	－１０
比較例２－１	圧延後	－５
比較例２－２	圧延後	０
比較例３	圧延後	７．５
比較例４－１	圧延後	０
比較例４－２	圧延後	０
比較例４－３	圧延後	０
比較例５－１	圧延後	０
比較例５－２	圧延後	０
比較例５－３	圧延後	０
比較例５－４	圧延後	０
比較例６	圧延後	０

【００８３】
　　表４から判るように、実施例サンプルはいずれも、極密度のピークが１０°以上または
－１０°以下にあり、ピークのシフト量（０°からのずれ）が１０°以上となっている。
これに対して、スタート材および比較例サンプルはいずれも、極密度のピークが－５°～
７．５°の間にあり、ピークのシフト量が１０°未満となっている。
【００８４】
　　・金属組織観察
　　図８は、ＺＫ６０材の組織観察結果を示す。図８（ａ）はＺＫ６０スタート材の光学顕
微鏡観察結果であり、図８（ｂ）は実施例１－１サンプルの光学顕微鏡観察結果であり、
図８（ｃ）は実施例２－１サンプルの光学顕微鏡観察結果であり、図８（ｄ）は実施例２
－１サンプルのＳＥＭ観察結果である。
　　図９は、ＡＺ３１材の組織観察結果を示す。図９（ａ）はＡＺ３１スタート材の光学顕
微鏡観察結果であり、図９（ｂ）は比較例５－３サンプルの光学顕微鏡観察結果であり、
図９（ｃ）は比較例４－３の光学顕微鏡観察結果である。
　　図１０は、ＺＫ６０材のＳＥＭによる組織観察結果を示す。図１０（ａ）は実施例２－
１サンプルに溶体化処理と時効処理を施したサンプルのＳＥＭ観察結果であり、図１０（
ｂ）は比較例３サンプルに溶体化処理と時効処理を施したサンプルのＳＥＭ観察結果であ
り、図１０（ｃ）は図１０（ａ）の黒枠部を拡大したＳＥＭ観察結果を示す。
　　図８～図１０の何れにおいても、写真の左から右に向かう方向が圧延方向（ＲＤ）であ
り、下から上に向かう方向が圧延面法線方向（ＮＤ）である。
【００８５】
　　図８および図９からＡＺ３１の比較例サンプルには多くの双晶が観察されるのに対して
、ＺＫ６０の実施例サンプルでは双晶はあまり観察されないことがわかる。
　　また、図１０より、実施例２－１サンプルに溶体化処理と時効処理を施したサンプルお
よび比較例３サンプルに溶体化処理と時効処理を施したサンプルのどちらにもZn_2Zr
相が多く析出しているのが認められる。一方、実施例２－１には、図１０（ｃ）に矢印で

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示すように細い棒状析出物Ｍｇ₄Ｚｎ₇（β１'相）が多く認められるが比較例３ではＭ
ｇ₄Ｚｎ₇はほとんど認められなかった。

【００８６】

・引張り試験

　実施例２－１、比較例３、比較例４－３および比較例６のサンプルについて、溶体化処
理と時効処理を施した後に引張り試験を実施した。

　図１１は、引張り試験に用いた試験片の形状および寸法を示す。ワイヤ放電加工機（ＥＤＭ
）を用いてそれぞれのサンプルから切り出した。

　引張り試験片はその長手方向（引張り方向）が圧延方向（ＲＤ方向）、ＲＤ方向から４５
°方向、圧延幅方向（ＴＤ方向）となるよう３方向のサンプルを切り出し、放電加工層の
影響を取り除くために、耐水エメリー紙＃２０００で研磨した。

　引張り試験の初期ひずみ速度は１．６７×１０⁻³ s⁻¹とし、室温大気中にてそれぞ
れの方向について試験した。試験は、それぞれの方向について、３本以上行い、この結果
から、０．２％耐力の最大値、最小値および平均値と伸びの最大値、最小値および平均値
とを求めた。

【００８７】

　図１２は引張り試験結果を示すグラフであり、図１２（ａ）は０．２％耐力を示し、図
１２（ｂ）は伸びを示す。

　図１２から判るように、０．２％耐力については、何れの方向においても実施例２－１
が、比較例３、比較例４－３および比較例６のいずれよりも高い値（すなわち、高強度）
となっている。

【００８８】

　伸び値については、実施例２－１が最も低くなっているが、それでも概ね１０％程度の
伸びを示していることから、いずれのサンプルも実用上問題のない延性を有することが判
る。

【００８９】

・成形試験

　厚さ０．９ｍｍの同じ厚さを有する実施例２－１、比較例３および比較例６について、
成形試験を実施した。

　なお、実施例２－１については、成形性の優れた状態（すなわち、成形加工を行うこと
を意図した状態）である、溶体化処理後で時効処理を行っていないサンプルを用いた。

【００９０】

　図１３は成形試験機の概略図である。

　ダイス肩半径が４．０ｍｍで中心部に直径１７ｍｍの空間を有するダイ１２と、中心に
直径１７ｍｍの空間を有するホルダー１４の間に試験片（ブランク）１０を配置し、ヒー
ター１６により試験片を１００℃から２００℃の所定温度に保持した後、ポンチ径１５ｍ
ｍのポンチ１８を上方から下方に１０ｍｍ／分（すなわち、成形速度１０ｍｍ／分）で押
し込んだ。

　ポンチ１８のポンチ肩半径は２．０ｍｍであった。また、試験片１０は直径２５ｍｍ（
従って絞り比は１．６７一定）、厚さ０．９ｍｍであり、実施例２－１、比較例３および
比較例６のサンプルより切り出して作製した。実施例２－１のサンプルについては、絞り
成形により生ずるカップの外側が異周速圧延の周速の速い側となるように試験片１０を配
置した。

　また、成形試験時に潤滑剤として二硫化モリブデンを用いた。

【００９１】

　表５は成形試験結果を示す。表５は、絞り比１．６７で問題なく成形できたサンプルを
「○」で示し、成形はできたもののクラックが認められたサンプルを「△」で示し、成形
中に破壊したサンプルを「×」で示す。

　図１４は成形試験後のサンプル評価結果を例示する写真であり、図１４（ａ）は、評価
結果が「×」であった、試験片の保持温度を１００℃とした成形試験後の実施例２－１サ

ンプルを示し、図１４（ｂ）は、評価結果が「△」であった、試験片の保持温度を１５０
℃とした成形試験後の比較例３サンプルを示し、図１４（ｃ）は、評価結果が「○」であ
った、試験片の保持温度を１２５℃とした成形試験後の実施例２－１サンプルを示す。
【００９２】
【表５】

保持温度（℃）	実施例２－１	比較例３	比較例６
２００		○	○
１７５	○	○○	○
１５０	○	×△	△△
１２５	○△		××
１００	××		

　　　　　　　○：良好　　　　△：クラックあり　　　×：破断
【００９３】
　比較例３が１５０℃で既に成形できないサンプルが生じ、また比較例６が１５０℃でク
ラックを生じ、１２５℃では既に成形できなかったのに対し、実施例２－１は温度が１２
５℃でも成形することができた。
　従って、実施例２－１は、比較例３および比較例６と比べ、顕著に優れた成形性を示し
た。
【符号の説明】
【００９４】
　１　高周速圧延ロール、２　低周速圧延ロール、３　マグネシウム合金材、１０　試験
片（ブランク）、１２　ダイ、１４　ホルダー、１６　ヒーター、１８　ポンチ

【図１】
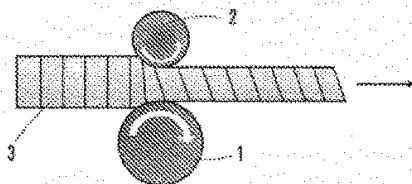
【図２】
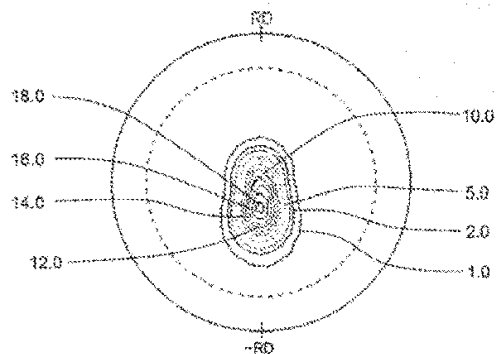
【図３】
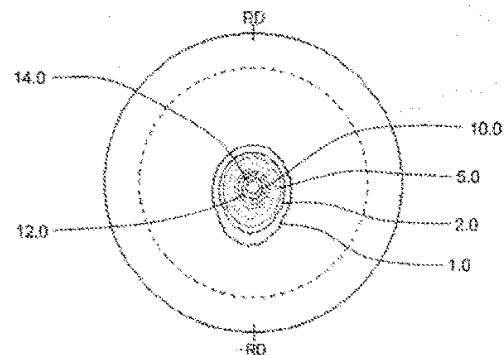
【図4】
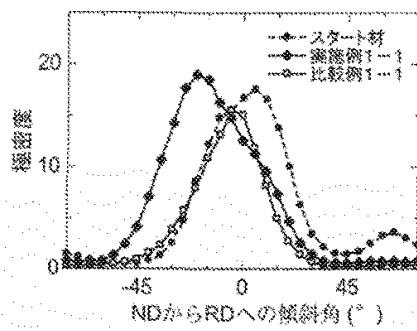
【図6】
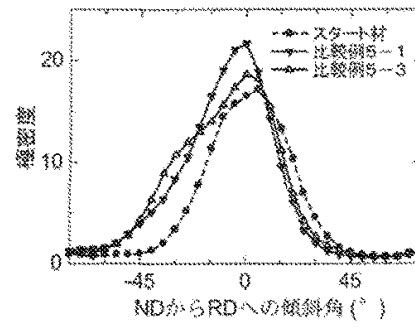
【図5】
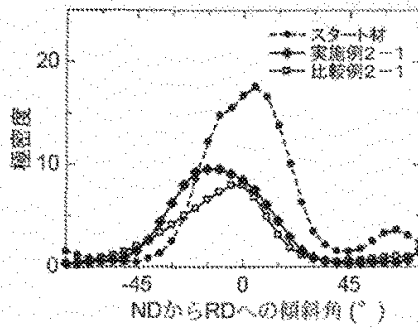
【図7】
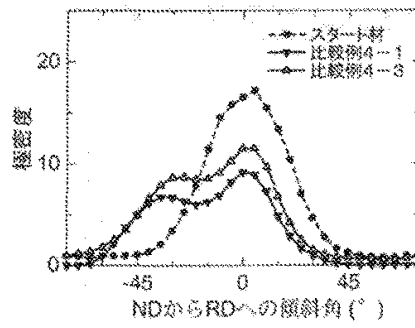
【図8】
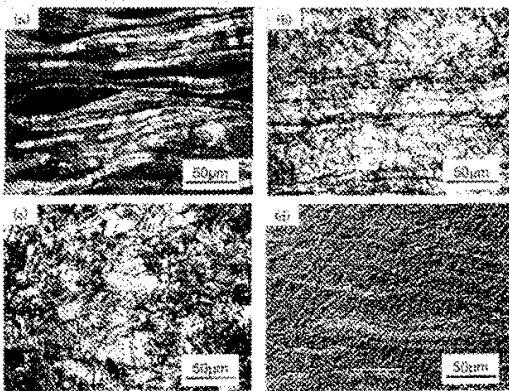
【図9】
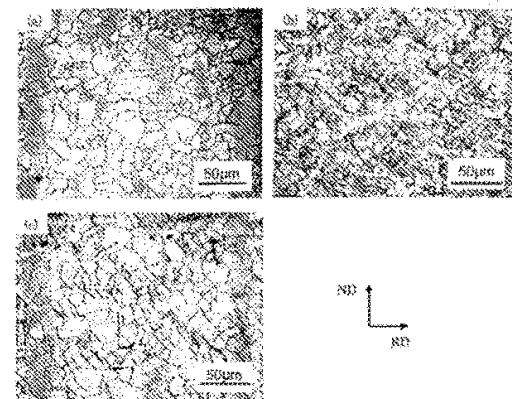
【図１０】
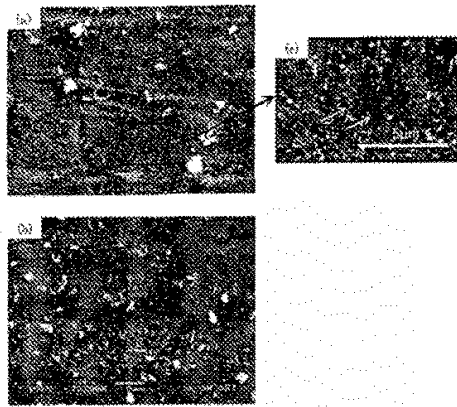
【図１１】
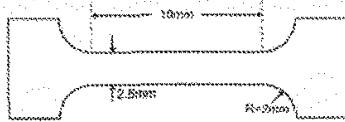
【図１３】
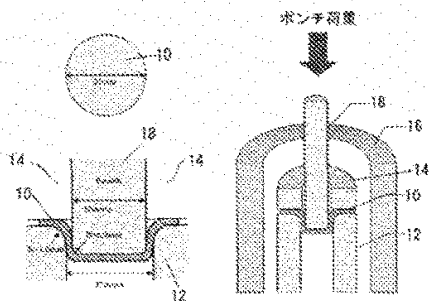
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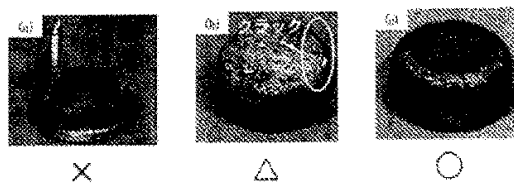
【図１２】
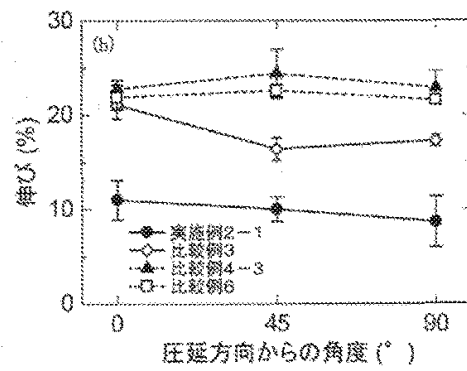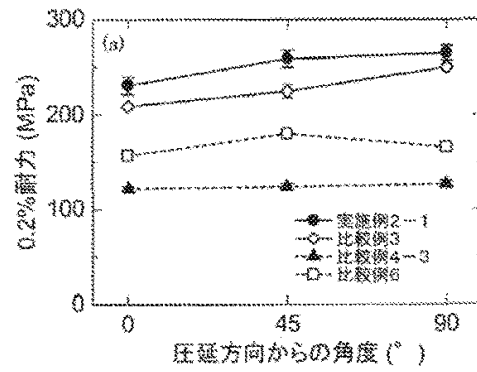
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(51)Int.Cl.	FI			テーマコード (参考)
	C22F	1/00	630H	
	C22F	1/00	630J	
	C22F	1/00	660Z	
	C22F	1/00	661Z	
	C22F	1/00	631Z	
	C22F	1/00	694Z	
	C22F	1/00	694A	
	C22F	1/00	694B	
	C22F	1/00	691B	
	C22F	1/00	691C	
	C22F	1/00	692A	
	C22F	1/00	683	
	C22F	1/00	623	
	C22F	1/00	684C	

フロントページの続き

(54) CASTING MAGNESIUM ALLOY AND PROCESS FOR PRODUCTION OF CAST MAGNESIUM ALLOY

(57)   A magnesium alloy for casting according to the present invention is **characterized in that**, when the entirety is taken as 100% by mass, it includes copper (Cu) in an amount of from 0.5% by mass or more to 10% by mass or less, calcium (Ca) in an amount of from 0.01% by mass or more to 3% by mass or less, and the balance comprising magnesium (Mg) and inevitable impurities.

Since the magnesium alloy for casting according to the present invention includes Cu whose heat conductivity is high in a predetermined amount, it is good in terms of heat-conducive ability. The heat-conductive ability is improved by carrying out heat treatment. Moreover, in the magnesium alloy for casting according to the present invention being in as-cast state, grain-boundary crystallized substances including Cu and Ca constitute three-dimensional networks in grain boundaries between Mg crystalline grains. In the network-shaped grain-boundary crystallized substances, grain-boundary sliding, which becomes active when they become high temperature, is suppressed, and thereby high-temperature strength and creep resistance improve.

Fig.4B

Mg–3%Cu–0.5%Ca (#1,#13)

25μm

EP 2 088 217 A1

ECOMETAL-002258
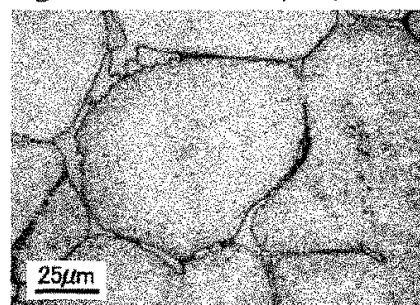
Description

TECHNICAL FIELD

5   **[0001]**   The present invention is one which relates to a magnesium alloy for casing, magnesium alloy which is suitable for service under high temperature.

BACKGROUND ART

10   **[0002]**   Magnesium alloy, which is much lightweight than aluminum alloy is, is about to come to be used widely for aircraft material, vehicle material, and the like, from the viewpoint of weight saving. However, in magnesium alloy, since the strength and heat resistance are not sufficient depending on applications, further improvement of the characteristics has been sought.
       [0003]   For example, in Japanese Unexamined Patent Publication (KOKAI) Gazette No. 2005-54,233, a magnesium
15   alloy that possesses heat resistance is disclosed. Concretely speaking, it is a magnesium alloy that includes aluminum (Al) in an amount of 4-9% by mass, copper (Cu) in an amount of 1-5% by mass, zinc (Zn) in an amount of 4% by mass or less, and beryllium (Be) in an amount of 0.001-0.01% by mass, and that is provided with a metallic structure in which Mg-Al-Cu system compounds are scattered in the mother-phase Mg.
       [0004]   Moreover, as a general magnesium alloy, AZ91D (ASTM code) is present, for instance. Although AZ91D is
20   good in terms of the mechanical characteristics and castability, the heat conductivity of AZ91D is 73 W/mK approximately and is extremely low compared with the heat conductivity of pure magnesium (167 W/mK). Accordingly, when AZ91D is used in member whose service environment is high temperature, or in member that generates heat in service, the radiation of heat cannot be carried out satisfactorily, and thereby thermal deformation might occur in the member. In particular, when a magnesium alloy whose heat conductivity is low is used as a magnesium alloy that is used in a cylinder
25   head or cylinder block of internal-combustion engine, the cylinder head undergoes thermal deformation, or heat dwells within the cylinder block so that the thermal deformation of cylinder bores augments, and thereby adverse affects, such as increased friction and declined airtightness, occur. Consequently, a magnesium alloy has been sought, magnesium alloy in which the radiation of heat is carried out satisfactorily by possessing a high heat conductivity, and magnesium alloy which is thereby suitable for usage under high temperature.

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DISCLOSURE OF THE INVENTION

       [0005]   In view of the aforementioned problematic issues, it is an object for the present invention to provide a magnesium alloy for casting, magnesium alloy which is suitable for usage under high temperature. Moreover, it is an object to provide
35   a production method of cast product, which comprises that magnesium alloy for casting.
       [0006]   As a result of wholehearted studies, the present inventors found out that it is possible to improve the heat-conductive ability of magnesium alloy by letting it contain copper whose heat conductivity is high in an adequate amount along with calcium, and then arrived at completing the present invention based on this.
       [0007]   Specifically, a magnesium alloy for casting according to the present invention is **characterized in that**, when
40   the entirety is taken as 100% by mass, it includes: copper (Cu) in an amount of from 0.5% by mass or more to 10% by mass or less; calcium (Ca) in an amount of from 0.01% by mass or more to 3% by mass or less; and the balance comprising magnesium (Mg) and inevitable impurities. In this instance, it is preferable that the copper (Cu) can be from 1% by mass or more to 5% by mass or less.
       [0008]   In an as-cast state (hereinafter being abbreviated to as an "as-cast material"), the magnesium alloy for casting
45   according to the present invention that includes Cu and Ca possesses a metallic structure that is constituted of Mg crystalline grains including Mg, and grain-boundary crystallized substances including Cu and Ca and being crystallized as three-dimensional network shapes (three-dimensionally mesh constructions) in grain boundaries between the Mg crystalline grains. By means of the grain-boundary crystallized substances that take on three-dimensionally mesh con-structions, grain-boundary sliding, which becomes active especially when becoming high temperature, is suppressed,
50   and thereby high-temperature strength and creep resistance at high temperature improve. And, it was understood newly that, in the magnesium alloy for casting according to the present invention, the heat conduction between the Mg crystalline grains is less likely to be hindered even when the grain-boundary crystallized substances are crystallized as network shapes by letting the present magnesium alloy contain copper whose heat conductivity is high in a predetermined amount as an alloying element.
55   **[0009]**   Moreover, in a heat-treated state in which the aforementioned as-cast material is treated with heat (hereinafter being abbreviated to as a "heat-treated material"), the magnesium alloy for casting according to the present invention has a metallic structure that is constituted of Mg crystalline grains including Mg, and granular compounds including Cu and being dispersed as granular shapes in grain boundaries between the Mg crystalline grains. The grain-boundary

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crystallized substances that are crystallized as network shapes in the grain boundaries between the Mg crystalline grains in the as-cast material are dispersed granularly in the grain boundaries between the Mg crystalline grains by means of heat treatment. Consequently, the contact areas between the Mg crystalline grains in the grain boundaries augment, and thereby heat conductivity improves. Moreover, even being a heat-treated material, the high-temperature strength and creep resistance at high temperature are less likely to lower when it contains Cu and Ca in the aforementioned predetermined ranges.

[0010]   Moreover, it is preferable that the magnesium alloy for casting according to the present invention can include aluminum (Al) in an amount of 10% by mass or less, or further 3% by mass or less. In the magnesium alloy for casting according to the present invention, the mechanical strengths of the magnesium alloy at room temperature and high temperature are improved by further including Al.

[0011]   Moreover, it is even allowable that the magnesium alloy for casting according to the present invention can further include manganese (Mn) in an amount of 1% by mass or less. In the magnesium alloy for casting according to the present invention, the creep resistance, the corrosion resistance, the castability, and the like, are improved by including Mn, in addition to the mechanical strengths at room temperature and high temperature.

[0012]   Moreover, a production method of magnesium-alloy cast product according to the present invention is a process for producing cast product comprising the magnesium alloy for casting according to the present invention. The production method of magnesium-alloy cast product according to the present invention is **characterized in that** it includes:

a molten-metal pouring step of pouring an alloy molten metal into a casting mold, the alloy molten metal including: copper (Cu) in an amount of from 0.5% by mass or more to 10% by mass or less; calcium (Ca) in an amount of from 0.01% by mass or more to 3% by mass or less; and the balance comprising manganese (Mg) and inevitable impurities; when the entirety is taken as 100% by mass; and
a solidifying step of solidifying the alloy molten metal after the molten-metal pouring step by cooling it.

[0013]   It is even allowable that the production method of magnesium-alloy cast product according to the present invention can include, after said solidifying step, a heat-treating step of granulating crystallized substances including Cu in grain boundaries between Mg crystalline grains including Mg.

[0014]   Hereinafter, "% by mass" might be abbreviated to "%" simply (however, [%], the units of "0.2% proof stress" and "elongation," does not mean "% by mass"). Note that any one of the respective alloying elements' contents is their proportions when the entire magnesium alloy for casting is taken as 100% by mass.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015]   Fig. 1 is a graph for illustrating the changes of heat conductivities with respect to Al contents in magnesium alloys that include Cu and Ca at least.

[0016]   Fig. 2 is a graph for illustrating the changes of heat conductivities with respect to Al/Cu values (mass ratio) in magnesium alloys that include Cu and Ca at least.

[0017]   Fig. 3 is a graph for illustrating the changes of tensile strengths and elongations with respect to Ca contents in magnesium alloys that include Cu and Ca at least.

[0018]   Fig. 4A and Fig. 4B are photographs for substituting for drawings that show the metallic structure of Mg-3%Cu-0.5%Ca alloy, and are a photograph (A) with low magnification and a photograph (B) with high magnification, respectively.

[0019]   Fig. 5A and Fig. 5B are photographs for substituting for drawings that show the metallic structure of Mg-3%Cu-0.2%Ca-3%Al alloy, and are a photograph (A) with low magnification and a photograph (B) with high magnification, respectively.

[0020]   Fig. 6A and Fig. 6B are photographs for substituting for drawings that show the metallic structure of Mg-3%Cu-3%Ca-3%Al-0.5%Mn alloy, and are a photograph (A) with low magnification and a photograph (B) with high magnification, respectively.

[0021]   Fig. 7 is a graph for illustrating the change of tensile strengths with respect to Ca contents in magnesium alloys that include Cu and Ca at least.

[0022]   Fig. 8 is a graph for illustrating the change of elongations with respect to Ca contents in magnesium alloys that include Cu and Ca at least.

[0023]   Fig. 9 is a graph for illustrating the change of heat conductivities with respect to Al contents in magnesium alloys that include Cu and Ca at least.

[0024]   Fig. 10 is a graph for illustrating the changes of stress lowering magnitudes with respect to Al contents in magnesium alloys that include 3% Cu and 1% Ca.

[0025]   Fig. 11A through Fig. 11D are photographs for substituting for drawings that show the metallic structure of magnesium alloys including 3% Cu and 1% Ca, and show the metallic structures of magnesium alloys that further include Al in an amount of 0.5% (A), 2% (B), 4% (C) and 8% (D), respectively.

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[0026] Fig. 12 shows the analyzed results on Mg-3%Cu-1%Ca-1%Al alloy by means of electron-beam microanalysis (EPMA).

[0027] Fig. 13 is a graph for illustrating the changes of tensile strengths, 0.2% proof stresses and elongations with respect to Cu contents in magnesium alloys (as-cast materials) that include 1% Ca, 1% Al and 0.5% Mn.

[0028] Fig. 14 is a graph for illustrating the changes of tensile strengths, 0.2% proof stresses and elongations with respect to Cu contents in magnesium alloys (heat-treated materials) that include 1% Ca, 1% Al and 0.5% Mn.

[0029] Fig. 15 is a graph for illustrating the changes of stress lowering magnitudes with respect to Cu contents in magnesium alloys that include 1% Ca, 1% Al and 0.5% Mn.

[0030] Fig. 16 is a graph for illustrating the changes of tensile strengths with respect to Mn contents in magnesium alloys that include 3% Cu,1% Ca and 1% Al.

[0031] Fig. 17 is a graph for illustrating the changes of stress lowering magnitudes with respect to Mn contents in magnesium alloys that include 3% Cu,1% Ca and 1% Al.

[0032] Fig. 18A and Fig. 18B are photographs for substituting for drawings that show the metallic structure of Mg-3%Cu-1%Ca alloy, and are a photograph (A) with low magnification and a photograph (B) with high magnification.

[0033] Fig. 19 shows the analyzed results on Mg-3%Cu-1%Ca alloy by means of EPMA.

[0034] Fig. 20 is a photograph for substituting for a drawing that shows the metallic structure of heat-treated Mg-3%Cu-1%Ca alloy.

[0035] Fig. 21 shows the analyzed results on heat-treated Mg-3%Cu-1%Ca alloy by means of EPMA.

Best Mode for Carrying Out the Invention

[0036] Hereinafter, the best mode for carrying out the magnesium alloy for casting according to the present invention and the production method of magnesium-alloy cast product according to the present invention will be explained.

[0037] The magnesium alloy for casting according to the present invention is **characterized in that** it includes copper (Cu), calcium (Ca), and the balance comprising magnesium (Mg) and inevitable impurities.

[0038] In an as-cast material of the magnesium alloy for casting according to the present invention that includes Cu and Ca, at least Cu and Ca crystallize in crystalline grain boundaries, and thereby a network-shaped metallic structure (three-dimensional mesh construction) is formed. Note that, as a general magnesium alloy, although there has been a magnesium alloy to which a rare-earth element, or the like, is added for the improvement of heat resistance, the three-dimensional mesh construction is less likely to be formed in suchamagnesiumalloy. Therefore, it is desirable that the magnesium alloy for casting according to the present invention cannot include any rare-earth element virtually.

[0039] It is preferable that, when the entire magnesium alloy for casting is taken as 100% by mass, the content of Cu can be 0.5% by mass or more, or further 1% by mass or more; and it is preferable that it can be 10% by mass or less, or further 5% by mass or less, or 4% by mass or less. When the content of Cu is less than 0.5% by mass, the improvement effect of heat conductivity that results from adding Cu cannot be obtained satisfactorily. Although heat is likely to flow when Cu is abundant, when it surpasses 10% by mass, no greater improvement of heat conductivity can be expected, and accordingly that is not economical. Moreover, that is not preferable because creep resistance at high temperature lowers.

[0040] Note that, in Cu and Cu compounds, their coefficients of thermal expansion are low. Consequently, the magnesium alloy for casting according to the present invention exhibits a low coefficient of thermal expansion.

[0041] The magnesium alloy for casting according to the present invention includes Ca along with Cu. Ca also crystallizes in crystalline grain boundaries along with Cu, and thereby it also contributes to the formation of three-dimensional mesh construction. For example, Mg-Ca system compounds crystallize along with Mg-Cu system compounds, and thereby a more complete three-dimensional mesh construction in which discontinuous sections are present less is formed. Moreover, Ca possesses an anti-inflammation effect. When Ca is added to magnesium alloy, since the ignition temperature of the magnesium alloy rises, the combustion that might occur when turning magnesium alloy into molten metal is prevented. It has been known that, in the magnesium alloy (AZ91) that includes Ca in an amount of 0.5% by mass, the ignition temperature is high by about 300 °C, compared with that of AZ91 that does not include Ca. Consequently, in the magnesium alloy for casting according to the present invention as well, it is preferable that, when the entire magnesium alloy for casting is taken as 100% by mass, the content of Ca can be from 0.01% by mass or more to 3% by mass or less, or further from 0.5% by mass or more to 2% by mass or less. Although it is allowable that Ca can be added to the magnesium alloy even in a small amount, the mechanical properties, such as the tensile strength and elongation, have lowered when it surpasses 3% by mass.

[0042] Moreover, it is believed that intermetallic compounds, such as the Mg-Cu compounds and the Mg-Ca compounds, which crystallize as network shapes in crystalline grain boundaries in the magnesium alloy for casting according to the present invention, suppress the grain-boundary sliding within the magnesium alloy. Consequently, it seems that the magnesium alloy for casting according to the present invention demonstrates such good creep resistance that creep deformations, and the like, are less even in high-temperature regions.

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[0043] It is allowable that the magnesium alloy for casting according to the present invention can further include aluminum (Al). In the magnesium alloy for casting according to the present invention to which Al is added, since Mg-Al-Cu system compounds and Mg-Al-Ca system compounds crystallize in crystalline grain boundaries, the mechanical properties, such as the tensile strength and elongation, improve. Meanwhile, the addition of Al might bring about the decline of heat conductivity. Consequently, it is preferable that, when the entire magnesium alloy for casting is taken as 100% by mass, the content of Al can be 10% by mass or less; and further it is preferable that it can be 4% by mass or less, or 3% by mass or less; depending on applications, it is desirable that it cannot rather include Al. In the case where mechanical strength is needed along with high heat conductivity, it is allowable to set the Al content when the entire magnesium alloy for casting according to the present invention is taken as 100% by mass at 0.5% by mass at least.

[0044] Moreover, it is preferable that the content of Al can exhibit a mass ratio to Cu (Al/Cu) of being 1 or less. When it is 1 or less, high heat conductivity and high mechanical strength are compatible with each other.

[0045] Moreover, it is allowable that, when the entire magnesium alloy for casting is taken as 100% by mass, the magnesium alloy for casting according to the present invention can further include manganese (Mn) in an amount of 1% by mass or less. Mn is an element that solves into the base material of magnesium alloy to solution harden the magnesium alloy. In addition, Mn also produces an effect of removing Fe, one of impurities that become a cause of corrosion, by sedimentation. That is, in the magnesium alloy according to the present invention to which Mn is added, the corrosion resistance improves along with the mechanical strength. However, such effects are subtle when Mn is too less; but, even when it surpasses 1% by mass, no improvement of the effects can be expected, and accordingly that is not economical. Therefore, a preferable Mn content can be 0.1% by mass or more, or 0.2% by mass or more, or further 0.3% by mass or more; and moreover it can be 1% by mass or less, or 0.8% by mass or less, or further 0.7% by mass or less.

[0046] Moreover, it is allowable that, when the entire magnesium alloy for casting is taken as 100% by mass, the magnesium alloy for casting according to the present invention can further include strontium (Sr) in an amount of 1% by mass or less. The magnesium alloy according to the present invention to which Sr is added produces an effect of improving corrosion resistance in magnesium alloy including Ca. Consequently, Sr is suitable as an alloying element for improving the corrosion resistance of the magnesium alloy for casting according to the present invention. In addition, Sr improves the castability (molten-metal flowability, and the like) of magnesium alloy. A preferable Sr content can be from 0.01% by mass or more to 1% by mass or less, or further from 0.1% by mass or more to 1% by mass or less.

[0047] Moreover, it is allowable that, when the entire magnesium alloy for casting is taken as 100% by mass, the magnesium alloy for casting according to the present invention can further include barium (Ba) in an amount of 1% by mass or less. In the magnesium alloy according to the present invention to which Ba is added, the castability improves. A preferable Ba content can be from 0.01% by mass or more to 1% by mass or less, or further from 0.1% by mass or more to 1% by mass or less.

[0048] Note that the alloying elements, such as Mn, Sr and Ba, do not impair the network-shaped metallic structure of the magnesium alloy for casting according to the present invention even when they are added to it.

[0049] When the magnesium alloy for casting according to the present invention makes an as-cast material, although it has a metallic structure that is constituted of Mg crystalline grains including Mg, and grain-boundary crystallized substances including Cu and Ca and being crystallized as three-dimensional network shapes in grain boundaries between the Mg crystalline grains, granular compounds including Cu, for example, Mg-Cu system compounds, are dispersed in the grain boundaries between the Mg crystalline grains including Mg by carrying out heat treatment. That is, it is allowable that the magnesium alloy for casting according to the present invention can have a metallic structure that is constituted of Mg crystalline grains including Mg, and granular compounds including Cu and being dispersed as granular shapes in grain boundaries between the Mg crystalline grains. It has been known that performing an appropriate heat treatment to magnesium alloy improves the mechanical characteristics. In the magnesium alloy for casting according to the present invention that possesses the aforementioned composition, the heat conductivity is improved by granulating Cu compounds by means of heat treatment. Moreover, when the contents of the additive elements, such as Cu and Ca, fall in the aforementioned ranges, the decline of creep resistance after heat treatment is suppressed.

[0050] Beginning with the fields of space, military and aviation, the magnesium alloy for casting according to the present invention being explained as above can be used in various fields, such as automobiles and electric instruments. Moreover, as a member comprising the magnesium alloy for casting according to the present invention, the following can be given, taking advantage of its characteristics at high temperature: products being utilized in high-temperature environments, for example, component parts constituting compressor, pumps and various cases that become high temperatures in service; moreover, engine component parts being used under high temperature and high load, especially, cylinder heads, cylinder blocks and oil pans of internal-combustion engine, impellers for turbocharger of internal-combustion engine, transmission cases being used for automobile and the like, and so forth.

[0051] Moreover, the production method of magnesium-alloy cast product according to the present invention is a production method of cast product comprising the magnesium alloy for casting according to the present invention that has been described in detail as above. The production method of magnesium-alloy cast product according to the present invention includes a molten-metal pouring step, and a solidifying step. The molten-metal pouring step is a step of pouring

an alloy molten metal into a casting mold, the alloy molten metal including: copper (Cu) in an amount of from 0.5% by mass or more to 10% by mass or less; calcium (Ca) in an amount of from 0.01% by mass or more to 3% by mass or less; and the balance comprising manganese (Mg) and inevitable impurities; when the entirety is taken as 100% by mass. The solidifying step is a step of solidifying the alloy molten metal after the molten-metal pouring step by cooling it.

[0052]   The magnesium-alloy cast product is not limited to those made by ordinary gravity casting and pressure casting, but can even be those made by die-cast casting. Moreover, even the casting mold being utilized for the casting does not matter if it is sand molds, metallic molds, and the like. Since even the solidification rate (cooling rate) in the solidifying step is not limited in particular, it is allowable to properly select such an extent of solidification rate, which permits to form the three-dimensional mesh construction, depending on the size of ingots. Note that, when it is solidified at a usual solidification rate, the metallic structure possessing the three-dimensional mesh construction is obtainable.

[0053]   Moreover, it is even allowable that the production method of magnesium-alloy cast product according to the present invention can include, after the solidifying step, a heat-treating step of dispersing granular compounds including Cu in grain boundaries between Mg crystalline grains including Mg. In the heat-treating step, it is allowable to carry out a tempering treatment after quenching (or high-temperature working), tempering treatment which is specified by the thermal-refining code "T5" or "T6" that is used in the JIS standard. For example, it is allowable to subject an as-cast member being made of the magnesium alloy for casting according to the present invention to an age-hardening treatment at a temperature of 100-300 °C after subjecting it to a solution treatment at a temperature of from 400 °C or more to a eutectic temperature or less. More desirably, it is allowable to carry out the solution treatment at a temperature of 400-550 °C, or further at a temperature of 410-510 °C; and then to carry out the age-hardening treatment at a temperature of 150-250 °C. Moreover, it is allowable that the solution treatment can be carried out while holding it at the high temperature for 5-24 hours, or further for 5-10 hours. In addition, in the solution treatment, although it is cooled to a low temperature after it has been held at the high temperature, it is allowable that the cooling can be either air cooling or water cooling; or it is desirable to quench it by means of water cooling. Note that it is allowable to select an optimum temperature, time and cooling rate for the heat treatment by means of usual methods that have been carried out heretofore.

[0054]   So far, the embodiment modes of the magnesium alloy for casting and production method of magnesium-alloy cast product according to the present invention have been explained, however, the present invention is not one which is limited to the aforementioned embodiment modes. It can be conducted in various modes to which modifications, improvements, and the like, which one of ordinary skill in the art can carry out, are performed, within a range not departing from the scope of the present invention.

[0055]   Hereinafter, while giving examples of the magnesium alloy for casting and production method of magnesium-alloy cast product according to the present invention, the present invention will be explained in detail.

[0056]   Test specimens whose contents of alloying elements in magnesium alloys were varied were made in a quantity of plural pieces, and then the evaluation of the characteristics and the observation of the metallic structures, and so forth, were carried out.

[0057]   [Making of Test Specimens #1-#10]

[0058]   A chloride-system flux was coated onto the inner surface of a crucible being made of iron that had been preheated within an electric furnace, and then a weighed pure magnesium base metal, pure Cu, and pure Al, if needed, were charged into it and were then melted. Further, weighed Ca was added into this molten metal that was held at 750 °C (a molten-metal preparing step).

[0059]   After fully stirring this molten metal to melt the raw materials completely, it was held calmly at the same temperature for a while. The thus obtained alloy molten metal was poured into a metallic mold with a predetermined configuration (a molten-metal pouring step), and was then solidified in air atmosphere (a solidifying step), thereby casting test specimens (magnesium-alloy cast products) being labeled #1-#10. Note that the obtained test specimens had a size of 30 mm × 30 mm × 200 mm. The alloy compositions of the respective test specimens were specified in Table 1. Note that "Alloy Composition I" is the proportions of the respective components, which were weighed at the molten-metal preparing step, when the raw materials were taken as 100% as a whole; and that "Alloy Composition II" is the alloy compositions of the respective test specimens that were analyzed by means of fluorescent X-ray analysis; and that the balance is Mg.

[0060]   [Measurements of Heat Conductivity and Mechanical Strength]

[0061]   Regarding the test specimens being labeled #1-#10, the heat conductivities were found by means of laser flash method. Moreover, the tensile test by means of JIS Z 2241 (testing temperature: 25 °C) was carried out, thereby finding the tensile strengths and elongations. The test results are specified in Table 1 all together. In addition, a graph that exhibits the changes of the heat conductivities with respect to the Al contents is illustrated in Fig. 1; a graph that exhibits the changes of the heat conductivities with respect to the Al/Cu values (mass ratio) is illustrated in Fig. 2; and a graph that exhibits the changes of the tensile strengths and elongations with respect to the Ca contents is illustrated in Fig. 3, respectively.

[0062]

[TABLE 1]

Test Specimen	Alloy Composition I [%]*			Alloy Composition II (Analyzed Value) [%]*			Al/Cu	Heat Conductivity [W/mK]	Tensile Strength [MPa]	Elongation [%]
	Cu	Ca	Al	Cu	Ca	Al				
#1	3	0.5		2.9	0.34	0.0	0.0	154	113.71	3.84
#2	3	1	1	2.9	0.85	0.8	0.3	138	125.36	2.47
#3	3	1	2	2.9	0.82	1.8	0.6	123	121.19	2.53
#4	3	1	3	2.9	0.74	3.0	1.0	105	120.00	3.32
#5	3	1	4	2.7	0.75	4.1	1.5	90	135.28	3.26
#6	3	1	5	2.7	0.72	5.4	2.0	80	-	-
#7	3	1	7	2.7	0.61	8.3	3.1	62	132.11	1.61
#8	3	2	3	2.7	1.50	2.7	1.0	110	94.30	1.23
#9	5	1		4.2	0.78	0.0	0.0	151	103.40	1.81
#10	3	0.2	3	2.9	0.13	2.7	0.9	104	161.64	7.18
*: The balance is Mg.										

[0063]　From Fig. 1, it was understood that the heat conductivity lowers when the Al content increases. In particular, the magnesium alloys whose Al content was 3% by mass or less exhibited a high heat conductivity (100 W/mK or more). Moreover, from Fig. 2, it was understood that the smaller the Al/Cu value is the larger the heat conductivity becomes. In particular, in the case where the Cu content was equal to the Al content, or in the case where it surpassed the Al content, the magnesium alloys exhibited a high conductivity (100 W/mK or more).

[0064]　Ca contributes to the formation of the three-dimensional mesh structure in magnesium alloy; however, from Fig. 3, it was understood that the greater the Ca content becomes the more the mechanical characteristics tend to lower.

[0065]　[Observation of Metallic Structure]

[0066]　Three types of test specimens for observing metallic structure were made in the same manner as the afore-mentioned procedures. Each "Alloy Composition I" was set at Mg-3%Cu-0.5%Ca (equivalent to #1), Mg-3%Cu-0.2%Ca-3%Al (equivalent to #10), and Mg-3%Cu-3%Ca-3%Al-0.5%Mn (the units, "%," were all "% by mass").

[0067]　The observation of the metallic structures was carried out by observing cross sections, which were cut out of the respective test specimens, with a metallographic microscope. The metallic structures are shown in Fig. 4A-Fig. 6B. In any one of the test specimens, the three-dimensional mesh construction was confirmed, three-dimensional mesh construction which comprised intermetallic compounds that crystallized in crystalline grain boundaries. Therefore, it was understood that a magnesium alloy including Cu and Ca at least possesses the three-dimensional mesh construction. Note that it is believed that the compounds that crystallized in crystalline grain boundaries were Mg-Cu system compounds and Mg-Ca system compounds in Figs. 4A and B; that they were Mg-Al-Cu system compounds and Mg-Ca system compounds in Figs. 5A and B; and that they were Mg-Al-Cu system compounds and Mg-Ca system compounds in Figs. 6A and B.

[0068]　[Making of Test Specimens #11-#35]

[0069]　A chloride-system flux was coated onto the inner surface of a crucible being made of iron that had been preheated within an electric furnace, and then a weighed pure magnesium base metal, pure Cu, and pure Al and an Al-Mn alloy, if needed, were charged into it and were then melted. Further, weighed Ca was added into this molten metal that was held at 750 °C (a molten-metal preparing step).

[0070]　After fully stirring this molten metal to melt the raw materials completely, it was held calmly at the same tem-perature for a while. The thus obtained alloy molten metal was poured into a metallic mold with a predetermined con-figuration (a molten-metal pouring step), and was then solidified in air atmosphere (a solidifying step), thereby casting test specimens (magnesium-alloy cast products) being labeled #11-#35. Note that the obtained test specimens had a size of 30 mm × 30 mm × 200 mm. The alloy compositions of the respective test specimens were specified in Table 2. Note that "Alloy Composition I" is the proportions of the respective components, which were weighed at the molten-metal preparing step, when the raw materials were taken as 100% as a whole; and that "Alloy Composition II" is the alloy compositions of the respective test specimens that were analyzed by means of fluorescent X-ray analysis; and that the balance is Mg.

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[0071] Note that #13, #16-#21 and #32 are the same test specimens as those of #1, #2-7 and #9, respectively (see the remarks column in Table 2).

[0072] [Measurements of Heat Conductivity and Mechanical Strength]

[0073] Regarding the test specimens being labeled #11-#35, the heat conductivities were found by means of laser flash method. Moreover, the tensile test by means of JIS Z 2241 (testing temperature: 25 °C) was carried out, thereby finding the tensile strengths, elongations and 0.2% proof stresses. The test results are specified in Table 2 all together (with regard to the 0.2% proof stresses, see Table 3). In addition, a graph that exhibits the change of the tensile strengths with respect to the Ca contents is illustrated in Fig. 7; a graph that exhibits the change of the elongations with respect to the Ca contents is illustrated in Fig. 8; and a graph that exhibits the change of the heat conductivities with respect to the Al contents is illustrated in Fig. 9, respectively.

[0074]

[TABLE 2]

Test Specimen	Alloy Composition I [%]*				Alloy Composition II {%}*				Al/Cu	Heat Conductivity [W/mK]	Tensile Strength [MPa]	Elongation [%]	Remarks
	Cu	Ca	Al	Mn	Cu	Ca	Al	Mn					
#11	1	1			0.88	0.69	0.00	0.00	0.0	158	90	2.3	
#12	2	1	0.5		1.90	0.70	0.54	0.00	0.3	146	120	2.6	
#13	3	0.5			2.90	0.34	0.00	0.00	0.0	154	114	3.8	#1
#14	3	1			2.80	0.51	0.00	0.00	0.0	155	129	3.9	
#15	3	1	0.5		2.80	0.62	0.54	0.00	0.2	145	112	2.0	
#16	3	1	1		2.90	0.85	0.78	0.00	0.3	138	125	2.5	#2
#17	3	1	2		2.90	0.82	1.80	0.00	0.6	123	121	2.5	#3
#18	3	1	3		2.90	0.74	3.00	0.00	1.0	105	120	3.3	#4
#19	3	1	4		2.70	0.75	4.10	0.00	1.5	90	135	3.3	#5
#20	3	1	5		2.70	0.72	5.40	0.00	2.0	80	114	1.5	#6
#21	3	1	7		2.70	0.61	8.30	0.00	3.1	62	132	1.6	#7
#22	3	1	0.335	1	2.90	0.85	0.20	0.52	0.1	136	98	1.5	
#23	3	1	0.5	1.5	2.90	0.69	0.52	1.10	0.2	130	121	2.1	
#24	3	1	1	0.2	3.30	0.78	0.89	0.19	0.3	136	137	3.3	
#25	3	1	1	0.5	3.23	0.82	0.93	0.51	0.3	135	131	2.2	
#26	3	1	1	0.8	3.27	0.86	0.93	0.67	0.3	132	142	2.9	
#27	3	1	1	3	2.90	0.82	0.97	1.20	0.3	130	114	1.8	
#28	3	2			2.80	1.80	0.00	0.00	0.0	154	93	0.9	
#29	3	2	1		2.99	2.14	0.98	0.00	0.3	134	96	0.8	
#30	3	2	1	0.2	3.14	1.87	0.99	0.19	0.3	134	99	0.7	
#31	3	2	1	0.5	3.21	2.14	0.98	0.45	0.3	131	113	0.9	
#32	5	1			4.20	0.78	0.00	0.00	0.0	151	103	1.8	#9
#33	1	1	1	0.5	1.21	0.74	1.20	0.38	1.0	128	128	3.7	
#34	5	1	1	0.5	5.16	0.84	0.85	0.40	0.2	132	128	2.0	

(continued)

Test Specimen	Alloy Composition I [%]*				Alloy Composition II {%}*				Al/Cu	Heat Conductivity [W/mK]	Tensile Strength [MPa]	Elongation [%]	Remarks
	Cu	Ca	Al	Mn	Cu	Ca	Al	Mn					
#35	10	1	1	0.5	9.42	0.53	0.81	0.30	0.1	133	143	1.8	

[0075] Test Specimens #11, #14 and #32 were magnesium alloys that included Ca in an amount of 1%, but whose Cu contents differed one another. Test Specimens #25 and #33-35 were magnesium alloys that included Ca in an amount of 1%, Al in an amount of 1% and Mn in an amount of 0.5%, but whose Cu contents differed one another. The heat conductivities of these magnesium alloys exhibited lowering magnitudes of 9-39 W/mK, which were small relatively compared with that of the heat conductivity of pure magnesium (167 W/mK) that was measured by the aforementioned method. It was understood that it is especially preferable that the Cu content can be 0.8-4.5%.

[0076] Moreover, Fig. 7 and Fig. 8 are graphs that summarize the change of the tensile strengths in Test Specimens #11-#35 and the change of the elongations in them for the Ca contents. As the Ca amounts increased, both the tensile strengths and elongations tended to decline. In particular, it was understood that magnesium alloys that possess high mechanical characteristic and high heat conductivity simultaneously can be obtained by keeping the Ca amount down to 2.5% or less, or further down to 1.5% or less. Further, according to Test Specimens #13, #14 and #28 which included Cu in an amount of 3% and whose Ca contents differed one another, it was understood that even varying the Ca contents has no great affect on the heat conductivities when the Ca amount falls in a range of 0.3-2.0%.

[0077] Moreover, Fig. 9 is a graph that summarizes the change of the heat conductivities in Test Specimens #11-#35 for the Al contents. As the Al amounts increased, the heat conductivities tended to decline. That is, in order to obtain magnesium alloy that possesses high heat conductivity, it is understood that it is preferable to keep down the Al content as much as possible.

[0078] [Stress Relief Test]

[0079] Regarding Test Specimens #11-#35 given in Table 2, a stress relief test was carried out, thereby examining the magnesium alloys' creep resistance under high temperature. In the stress relief test, a process was measured, process in which stress that arose when load was applied to test specimen until it deformed to predetermined deformation magnitude decreased with time during the time of testing. Concretely speaking, in 200 °C air atmosphere, a compression stress of 100 MPa was loaded to the respective test specimens, and then that compression stress was lowered as the time elapsed so that the test specimens' displacement on that occasion could be kept constant. The stress lowering magnitudes after 1 hour from the beginning of the test, those after 10 hours therefrom and those after 40 hours therefrom; and stress lowering rates from after 20 hours and up to 40 hours are given in Table 3, respectively.

[0080]

[TABLE 3]

Test Specimen	Alloy CompositionII(Analyzed Value) [%]*				0.2% Proof Stress [MPa]	Stress Lowering Magnitude			Stress Lowering Rate	Remarks
	Cu	Ca	Al	Mn		0-1 h [MPa]	0-10 h [MPa]	0-40 h [MPa]	20-40 [MPa/h]	
#11	0.88	0.69	0.00	0.00	49	26	48	59	0.26	
#12	1.90	0.70	0.54	0.00	62	-	-	-	-	
#13	2.90	0.34	0.00	0.00	51	26	53	65	0.31	#1
#14	2.80	0.51	0.00	0.00	58	22	51	65	0.29	
#15	2.80	0.62	0.54	0.00	60	26	44	52	0.21	
#16	2.90	0.85	0.78	0.00	64	22	34	42	0.19	#2
#17	2.90	0.82	1.80	0.00	61	24	35	42	0.14	#3
#18	2.90	0.74	3.00	0.00	52	29	41	48	0.19	#4
#19	2.70	0.75	4.10	0.00	60	29	42	51	0.20	#5
#20	2.70	0.72	5.40	0.00	67	29	43	55	0.30	#6
#21	2.70	0.61	8.30	0.00	72	26	43	54	0.26	#7
#22	2.90	0.85	0.20	0.52	62	21	36	42	0.12	
#23	2.90	0.69	0.52	1.10	69	17	27	33	0.15	
#24	3.30	0.78	0.89	0.19	62	17	26	28	0.13	
#25	3.23	0.82	0.93	0.51	70	12	19	20	0.09	

(continued)

Test Specimen	Alloy Composition II (Analyzed Value) [%]*				0.2% Proof Stress [MPa]	Stress Lowering Magnitude			Stress Lowering Rate	Remarks
	Cu	Ca	Al	Mn		0-1 h [MPa]	0-10 h [MPa]	0-40 h [MPa]	20-40 [MPa/h]	
#26	3.27	0.86	0.93	0.67	69	13	18	21	0.15	
#27	2.90	0.82	0.97	1.20	70	14	20	23	0.10	
#28	2.80	1.80	0.00	0.00	69	25	50	61	0.31	
#29	2.99	2.14	0.98	0.00	68	13	27	37	0.15	
#30	3.14	1.87	0.99	0.19	75	12	20	24	0.08	
#31	3.21	2.14	0.98	0.45	75	11	18	23	0.20	
#32	4.20	0.78	0.00	0.00	68	26	52	64	0.17	#9
#33	1.21	0.74	1.20	0.38	58	14	18	24	0.17	
#34	5.16	0.84	0.85	0.40	75	17	24	27	0.08	
#35	9.42	0.53	0.81	0.30	85	16	29	34	0.17	

[0081] Fig. 10 is a graph that summarizes the changes of the stress lowering magnitudes after 40 hours from the beginning of the test in Test Specimens #14-#21, which included Cu in an amount of 3% and Ca in an amount of 1% but whose Al contents differed one another, for the Al contents. Magnesium alloy whose stress loweringmagnitude is small is good in terms of creep resistance at high temperature. According to Fig. 10, it was understood that good creep resistance was exhibited even at high temperature by setting the Al content to 0.5% or more, or further to 0.75% or more.

[0082] [Observation of Metallic Structure]

[0083] Four types of test specimens for observingmetallic structure were made in the same manner as the aforementioned procedures. Each "Alloy Composition I" was set at Mg-3%Cu-1%Ca-0.5Al (equivalent to #15), Mg-3%Cu-1%Ca-2%Al (equivalent to #17), Mg-3%Cu-1%Ca-4%Al (equivalent to #19), and Mg-3%Cu-1%Ca-8%Al (the units, "%," were all "% by mass").

[0084] The observation of the metallic structures was carried out by observing cross sections, which were cut out of the respectivetest specimens, with a metallographic microscope. The metallicstructures are shown in Fig. 11A-Fig. 11D. In Fig. 11A-11C, the three-dimensional mesh construction was confirmed, three-dimensional mesh construction which comprised intermetallic compounds that crystallized in crystalline grain boundaries. However, the three-dimensional mesh construction had come not to be seen as the Al contents increased. It is believed that the decrease of the three-dimensional mesh construction that was accompanied by the increase of Al had influence on the deterioration of the creep resistance. When taking the graph of Fig. 10 also into consideration, it is especially preferable that the Al content can be 4.5% or less.

[0085] [EPMA Analysis]

[0086] Regarding an Mg-3%Cu-1%Ca-1%Al (equivalent to #16), an analysis by means of electron-beam microanalysis (EPMA) was carried out. The results are shown in Fig. 12. Note that, in Fig. 12, the upper left photograph is the secondary electron-beam image (BEI) and the others are areal-analysis results that analyzed the elemental distributions in the regions of the secondary electron-beam image. It was understood that the magnesium alloy being labeled #16 possessed a metallic structure that comprised: Mg crystalline grains comprising mainly Mg; and grain-boundary crystallized substances being crystallized as three-dimensional network shapes in grain boundaries between the Mg crystalline grains, and including Cu, Ca and Al.

[0087] [Making of Heat-treated Test Specimen]

[0088] Aforementioned Test Specimens #14-#16, #23-#27, #29-#31 and #33-#35 (as-cast materials) were heat treated, thereby making Test Specimens #14a-#16a, #23a-#27a, #29a-#31a and #33a-#35a (heat-treated materials). The heat treatment was carried out as follows: the as-cast materials were heated to 410-510 °C for 5-24 hours and then water cooled (a solution treatment); and thereafter they were reheated to 150-250 °C for 1-10 hours (an age-hardening treatment).

[0089] Regarding the heat-treated materials as well, the heat conductivities, tensile strengths, elongations, 0.2% proof stresses and stress lowering magnitudes were measured in the same manner as aforementioned. The results are given in Table 4.

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[TABLE 4]

Test Specimen	Alloy Composition II (Analyzed Value) [%]*				Heat Conductivity [W/mK]	Tensile Strength [MPa]	Elongation [%]	0.2% Proof Stress [MPa]	Stress Lowering Magnitude			Stress Lowering Rate
	Cu	Ca	Al	Mn					0-1 h [MPa]	0-10 h [MPa]	0-40 h [MPa]	20-40 h [MPa/H]
#14a	2.80	0.51	0.00	0.00	163	130	4.2	61	22	51	66	0.18
#15a	2.80	0.62	0.54	0.00	157	136	3.2	76	22	46	58	0.24
#16a	2.90	0.85	0.78	0.00	146	161	2.6	98	20	31	42	0.28
#23a	2.90	0.69	0.52	1.10	154	143	4.4	62	31	51	61	0.22
#24a	3.30	0.78	0.89	0.19	142	179	3.4	112	10	20	29	0.33
#25a	3.23	0.82	0.93	0.51	144	176	2.7	111	8	19	28	0.30
#26a	3.27	0.86	0.93	0.67	146	175	2.4	113	9	18	27	0.25
#27a	2.90	0.82	0.97	1.20	150	157	2.1	98	11	25	36	0.24
#29a	2.99	2.14	0.98	0.00	134	148	1.5	93	8	17	25	0.25
#30a	3.14	1.87	0.99	0.19	140	145	1.2	102	8	17	27	0.43
#31a	3.21	2.14	0.98	0.45	142	151	1.4	115	7	18	29	0.33
#33a	1.21	0.74	1.20	0.38	138	191	5.1	83	17	26	32	0.18
#34a	5.16	0.84	0.85	0.40	148	144	2.1	87	17	41	52	0.24
#35a	9.42	0.53	0.81	0.30	145	182	4.2	106	13	39	54	0.35

[0091] When comparing the heat conductivities before the heat treatment with those after it, there were no test specimens whose heat conductivities were lowered by means of the heat treatment, and improvements of the heat conductivities by means of the heat treatment were appreciated in most of the test specimens. Moreover, from the measurement results on the heat conductivities of Test Specimens #16, #24-#27 and #16a, #24a-#27a, or from those of Test Specimens #29-#31 and #29a-#31a, the more Mn contents the test specimens had, the greater the heat conductivities were improved by means of the heat treatment.

[0092] Fig. 13 and Fig. 14 are graphs that summarize the change of the mechanical characteristics in the magnesium alloys, which included Ca in an amount of 1%, Al in an amount of 1% and Mn in an amount of 0.5% but whose Cu contents differed, for the Ca contents. Note that Fig. 13 illustrates those in the as-cast materials; and Fig. 14 illustrates those in the heat-treated materials. In any one of the test specimens, the mechanical characteristics were improved by means of the heat treatment.

[0093] Fig. 15 is a graph that summarizes the changes of the stress lowering magnitudes after 40 hours from the beginning of the test in the magnesium alloys, which included Ca in an amount of 1%, Al in an amount of 1% and Mn in an amount of 0.5% but whose Cu contents differed, for the Cu contents. In both the as-cast materials and heat-treated materials, the more the Cu contents were the more the creep resistances at high temperature tended to decline. Moreover, although the creep resistances at high temperature were declined by means of the heat treatment, it was understood that, not limited to those in the as-cast materials, the decline of creep resistance by means of heat treatment can be kept down by setting the Cu content to 3.5% by mass or less.

[0094] Fig. 16 is a graph that summarizes the changes of the tensile strengths in the magnesium alloys, which included Cu in an amount of 3%, Ca in an amount of 1% and Al in an amount of 1% but whose Mn contents differed, for the Mn contents. Despite the Mn contents, the tensile strengths after the heat treatment improved. Moreover, Fig. 17 is a graph that summarizes the changes of the stress lowering magnitudes after 40 hours from the beginning of the test in the magnesium alloys, which included Cu in an amount of 3%, Ca in an amount of 1% and Al in an amount of 1% but whose Mn contents differed, for the Mn contents. In the as-cast materials, the more the Mn contents were the more the creep resistances tended to improve. However, when containing it in excess of 1%, no improvement of creep resistances is appreciated, but the decline of creep resistances is predicted adversely. In addition, when the Mn content exceeded 1%, the creep resistances of the heat-treated materials declined greatly. Therefore, it is possible to say that an especially preferable Mn content can be 0.1-0.8%, or further 0.3-0.7%.

[0095] In Fig. 18A, Fig. 18B and Fig. 19-Fig. 21, the observation results on the metallic structures of Test Specimen #14 before and after the heat treatment, and the EPMA analysis results thereon. Fig. 18A and Fig. 18B show the metallic structure of the as-cast material. In Fig. 18A, the three-dimensional mesh construction was observed. In Fig. 18B with high magnification, the following were observed in the crystalline grain boundaries: portions whose contrasts were uniform (a part of them is specified with "P1"); and portions whose contrasts were striped shapes (a part of them is specified with "P2"). According to the EMPA analysis results shown in Fig. 19, it was understood that "P1" comprises Mg-Cu system compounds and "P2" comprises Mg-Ca system compounds. Moreover, it was understood that Cu and Ca, most of them, exist in the crystalline grain boundaries.

[0096] Meanwhile, Fig. 20 shows the metallic structure of one of the heat-treated materials (#14a). In the heat-treated material, granular compounds (a part of them is specified with "P3"), which had granular shapes and existed dispersedly, were appreciated. Moreover, like portions being specified with "P4," locations at which neighboring Mg crystalline grains contacted with each other, were appreciated abundantly. It is believed that heat-treated material comes to exhibit high heat conductivity by means of possessing such a metallic structure. According to the EMPA analysis results shown in Fig. 21, it was understood that "P3" comprises Cu system compounds including mainly Cu. In addition, it was understood that, although Cu, most of it, exists in the crystalline grain boundaries, the major part of Ca exists diffusedly in the Mg crystalline grains. This is definite from the facts that, when the areal-analysis results on Ca shown in Fig. 19 (as-cast material) is compared with the areal-analysis results on Ca shown in Fig. 21 (heat-treated material), the contrast is brighter as a whole in Fig. 21 than in the other (in the color photograph, Ca that is indicated in blue is dotted within the area that comprises Mg mostly and is indicated in black.)

Claims

1. A magnesium alloy for casting, the magnesium alloy being **characterized in that**, when the entirety is taken as 100% by mass, it includes:

   copper (Cu) in an amount of from 0.5% by mass or more to 10% by mass or less;
   calcium (Ca) in an amount of from 0.01% by mass or more to 3% by mass or less; and
   the balance comprising magnesium (Mg) and inevitable impurities.

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2. The magnesium alloy for casting as set forth in claim 1 further including aluminum (Al) in an amount of 10% by mass or less when the entirety is taken as 100% by mass.

3. The magnesium alloy for casting as set forth in claim 1 further including aluminum (Al) in an amount of 3% by mass or less when the entirety is taken as 100% by mass.

4. The magnesium alloy for casting as set forth in claim 1, wherein said copper (Cu) is from 1% by mass or more to 5% by mass or less.

5. The magnesium alloy for casting as set forth in claim 1 further including manganese (Mn) in an amount of 1% by mass or less when the entirety is taken as 100% by mass.

6. The magnesium alloy for casting as set forth in claim 1 having a metallic structure that is constituted of Mg crystalline grains including Mg, and grain-boundary crystallized substances including Cu and Ca and being crystallized as three-dimensional network shapes in grain boundaries between the Mg crystalline grains.

7. The magnesium alloy for casing as set forth in claim 1 having a metallic structure that is constituted of Mg crystalline grains including Mg, and granular compounds including Cu and being dispersed as granular shapes in grain boundaries between the Mg crystalline grains.

8. A cylinder head of internal-combustion engine, the cylinder head comprising the magnesium alloy for casting as set forth in claim 1.

9. A cylinder block of internal-combustion engine, the cylinder block comprising the magnesium alloy for casting as set forth in claim 1.

10. An oil pan of internal-combustion engine, the oil pan comprising the magnesium alloy for casting as set forth in claim 1.

11. An impeller for turbocharger of internal-combustion engine, the impeller comprising the magnesium alloy for casting as set forth in claim 1.

12. A transmission case comprising the magnesium alloy for casting as set forth in claim 1.

13. A production method of magnesium-alloy cast product, the production method being **characterized in that** it includes:

a molten-metal pouring step of pouring an alloy molten metal into a casting mold, the alloy molten metal including: copper (Cu) in an amount of from 0.5% by mass or more to 10% by mass or less; calcium (Ca) in an amount of from 0.01% by mass or more to 3% by mass or less; and the balance comprising manganese (Mg) and inevitable impurities; when the entirety is taken as 100% by mass; and
a solidifying step of solidifying the alloy molten metal after the molten-metal pouring step by cooling it.

14. The production method of magnesium-alloy cast product as set forth in claim 13 including, after said solidifying step, a heat-treating step of granulating crystallized substances including Cu in grain boundaries between Mg crystalline grains including Mg.

15. The production method of magnesium-alloy cast product as set forth in claim 14, wherein said heat-treating step is a step in which an age-hardening treatment is carried out at 100-300 °C after carrying out a solution treatment at 400-550 °C.
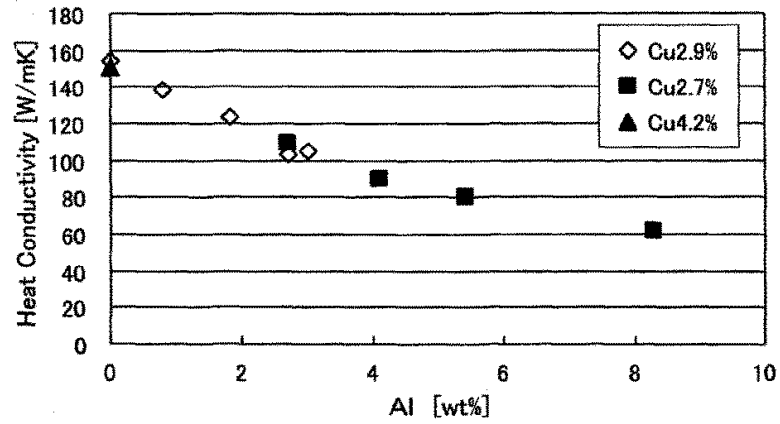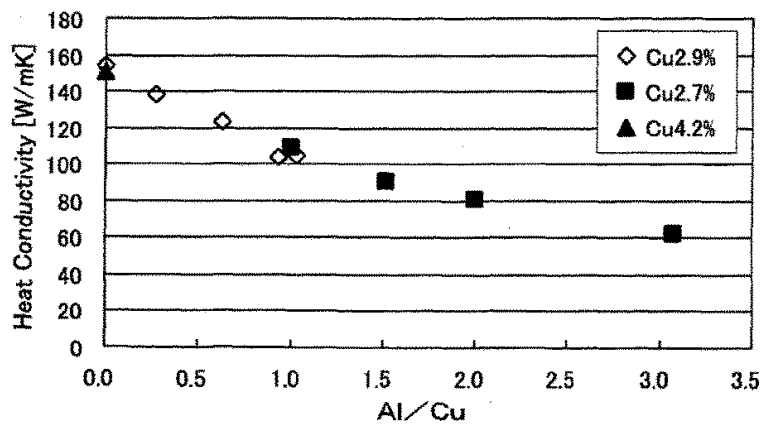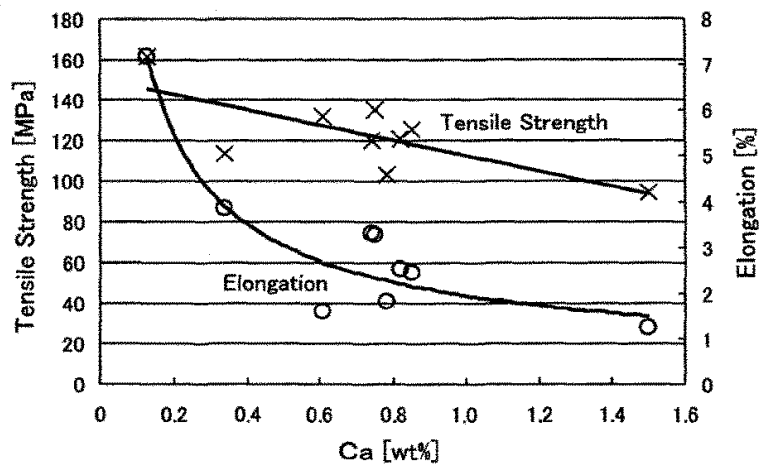
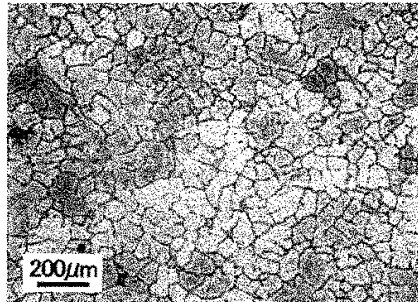16

Fig.1

Fig.2

Fig.3

Fig.4A

Mg-3%Cu-0.5%Ca (#1,#13)
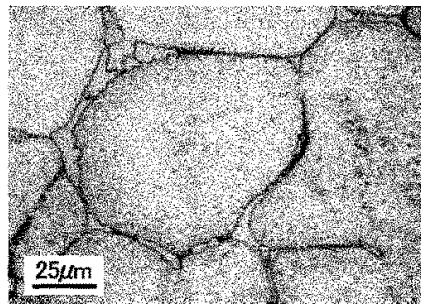

200μm

Fig.4B

Mg-3%Cu-0.5%Ca (#1,#13)

25μm

Fig.5A

Mg–3%Cu–0.2%Ca–3%Al (#10)

200μm
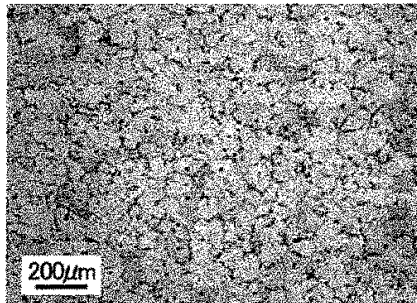
Fig.5B

Mg–3%Cu–0.2%Ca–3%Al (#10)

25μm
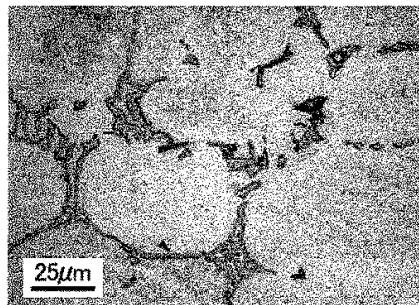
Fig.6A

Mg–3%Cu–3%Ca–3%Al–0.5%Mn

200μm
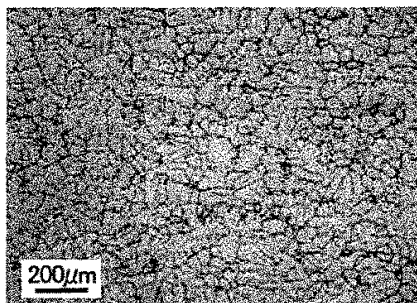
Fig.6B

Mg–3%Cu–3%Ca–3%Al–0.5%Mn

25μm
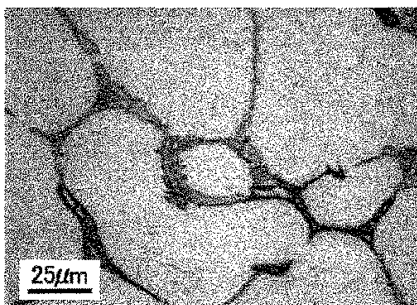
Fig.7
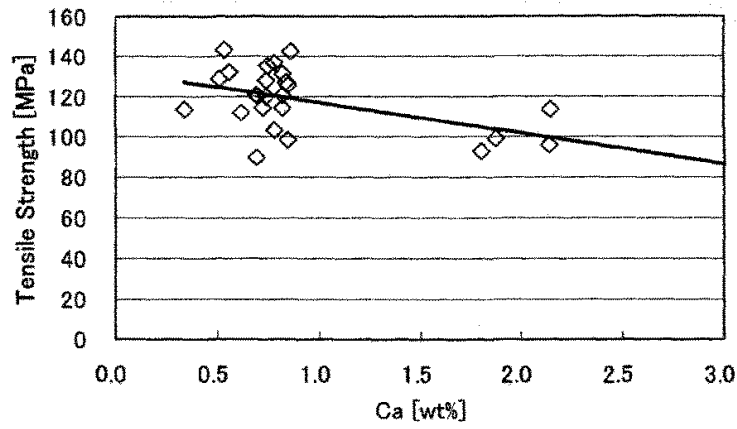
Fig.8
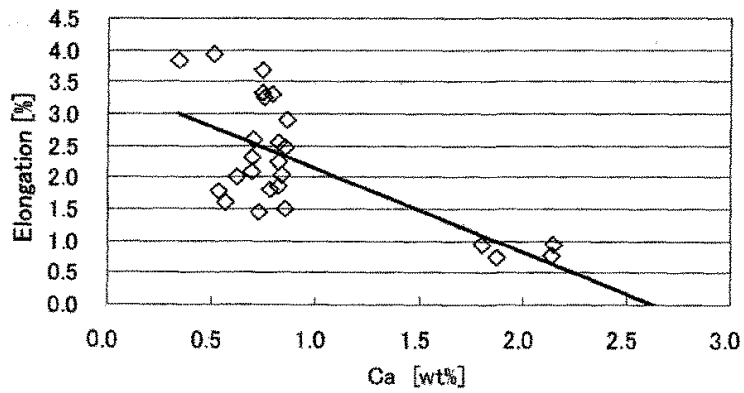
Fig.9
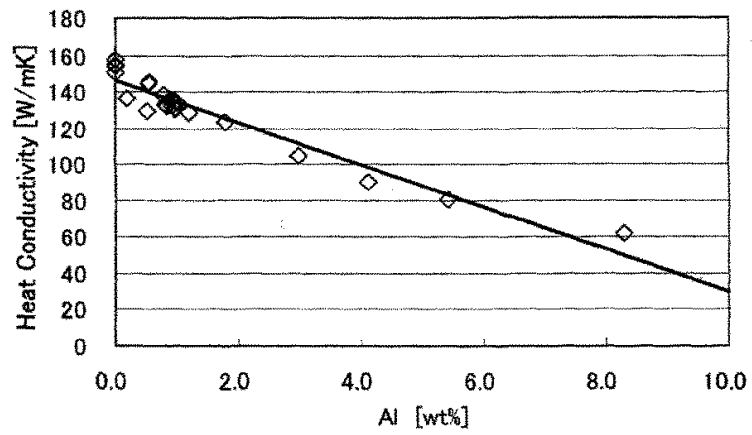
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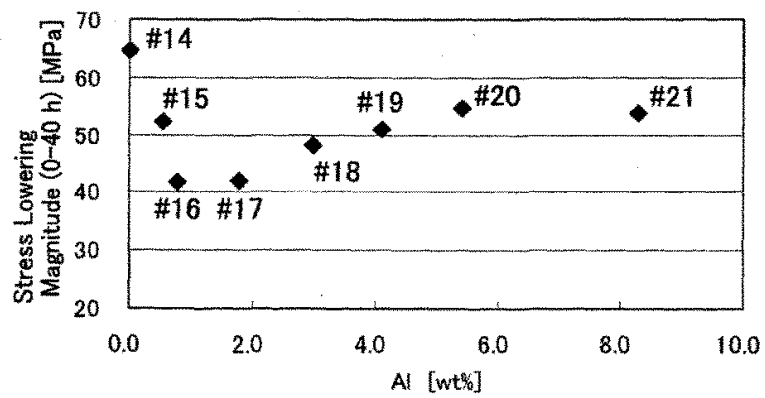
Fig.11A

Mg−3%Cu−1%Ca−0.5%Al (#15)

25μm
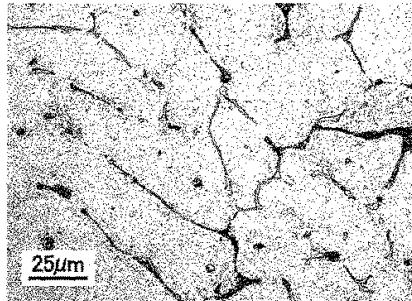
Fig.11B

Mg−3%Cu−1%Ca−2%Al (#17)

25μm
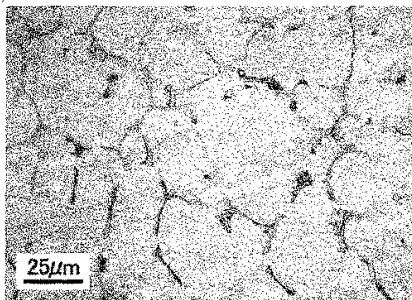
Fig.11C

Mg−3%Cu−1%Ca−4%Al (#19)

25μm
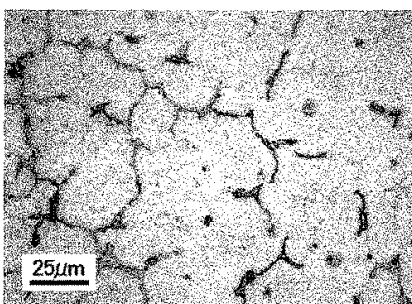
Fig.11D

Mg-3%Cu-1%Ca-8%Al

25μm
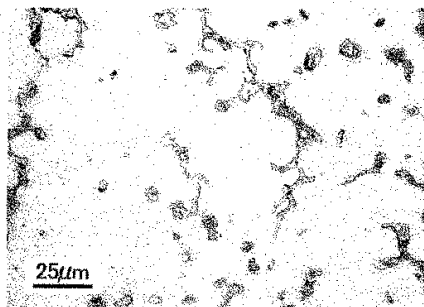
Fig.12
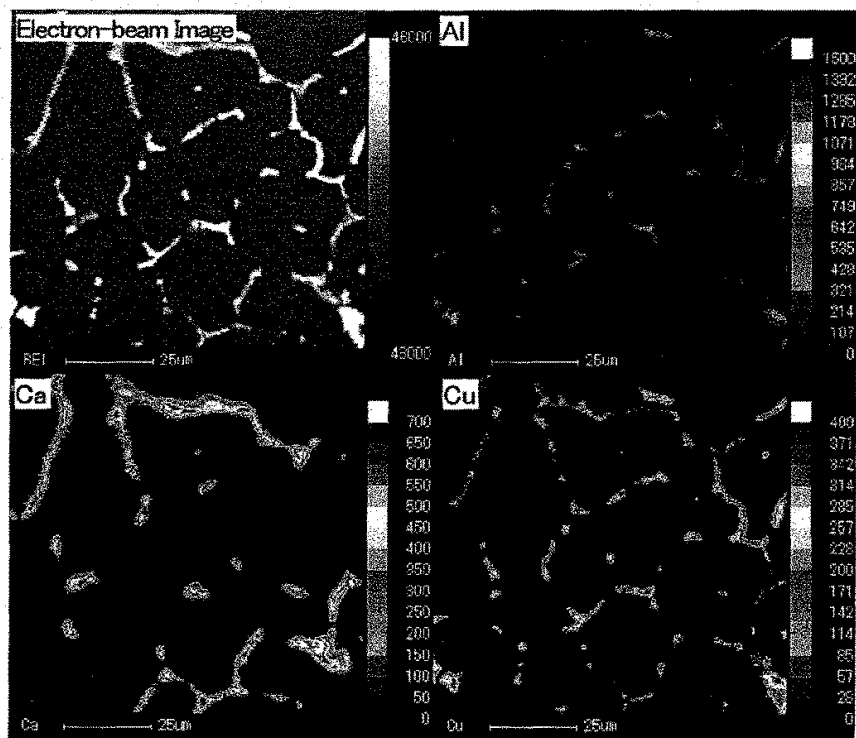
Fig.13
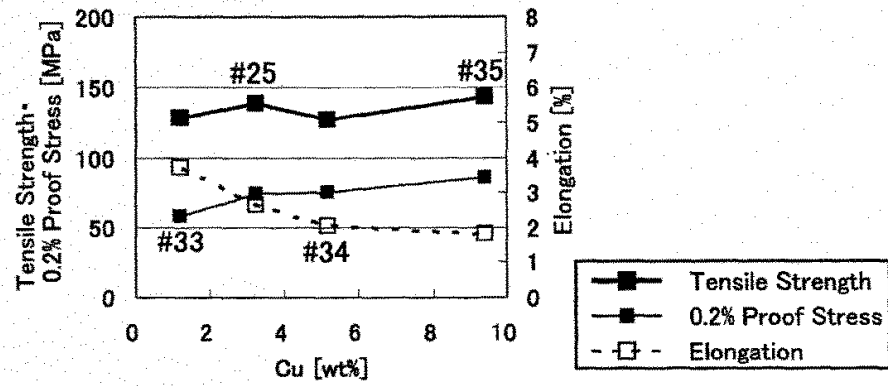
Fig.14
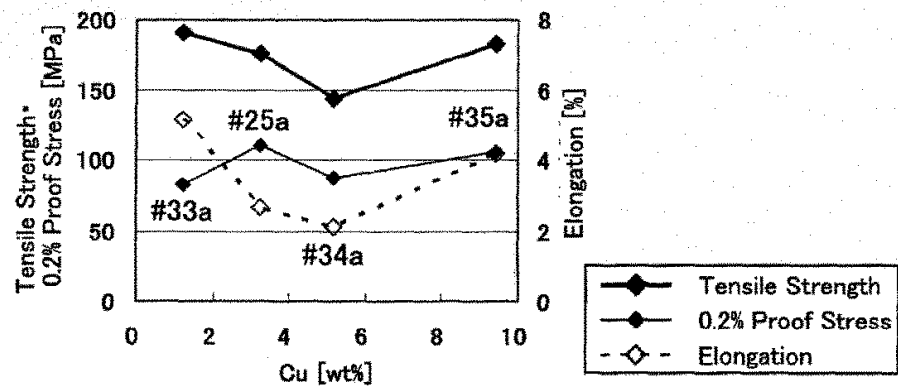
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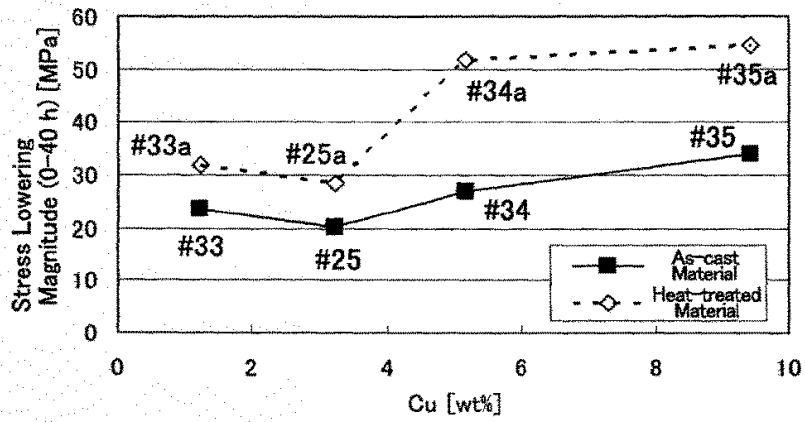
Fig.16
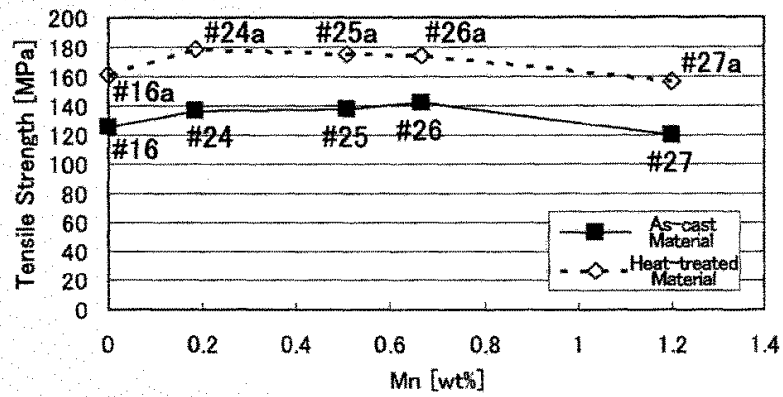
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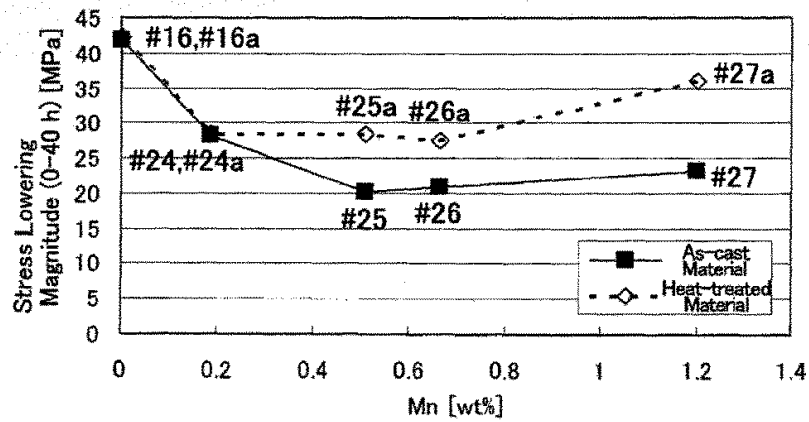
Fig.18A

Mg–3%Cu–1%Ca (#14)

25μm
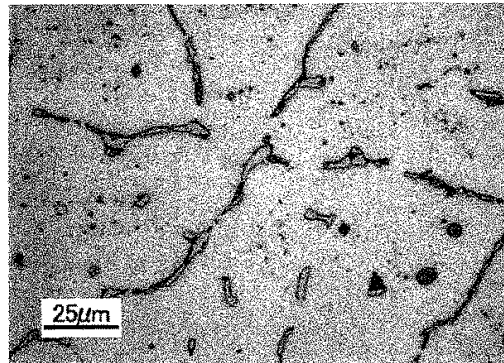
Fig.18B

Mg–3%Cu–1%Ca (#14)

P2

P1

10 μm
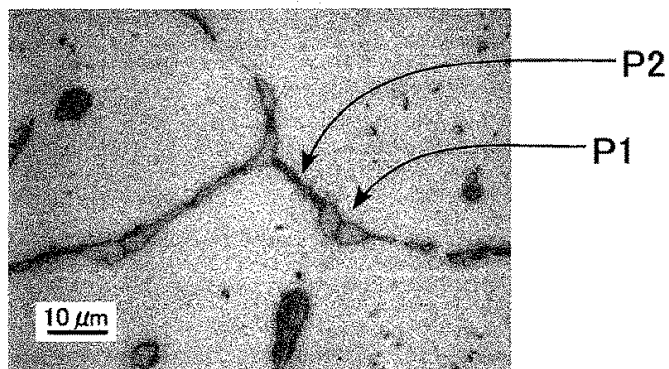
Fig.19

Fig.20

Mg-3%Cu-1%Ca (#14a)

25μm

P3

P4
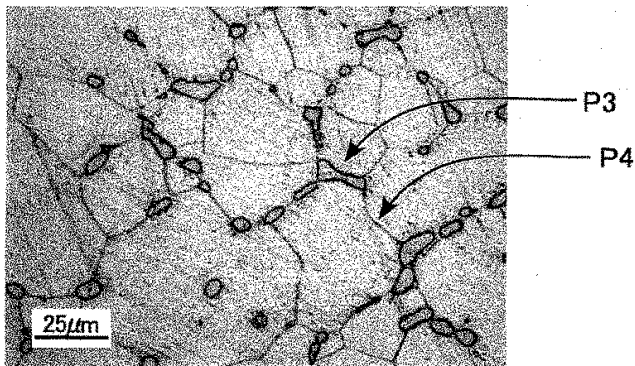
Fig.21
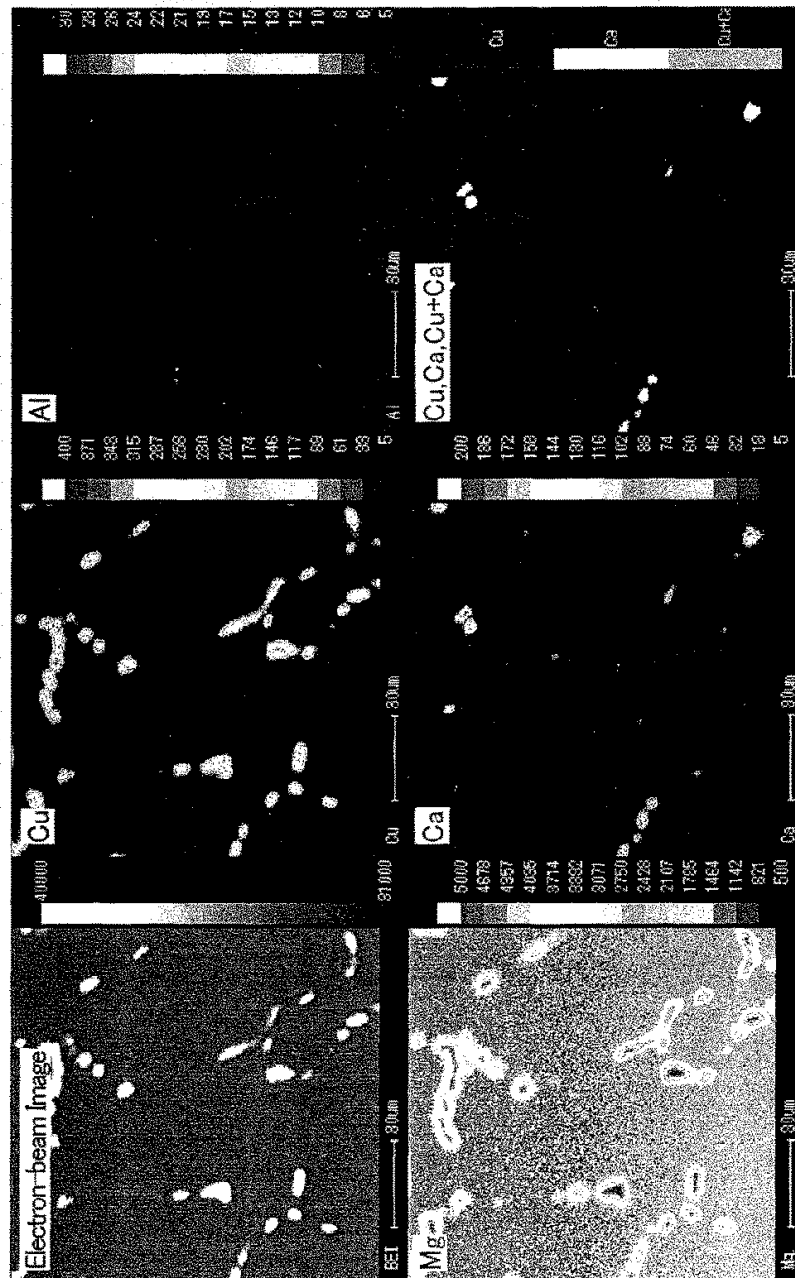
INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/071756

A. CLASSIFICATION OF SUBJECT MATTER

C22C23/00(2006.01)i, *C22C23/02*(2006.01)i, *C22F1/06*(2006.01)i, *F02B39/00*
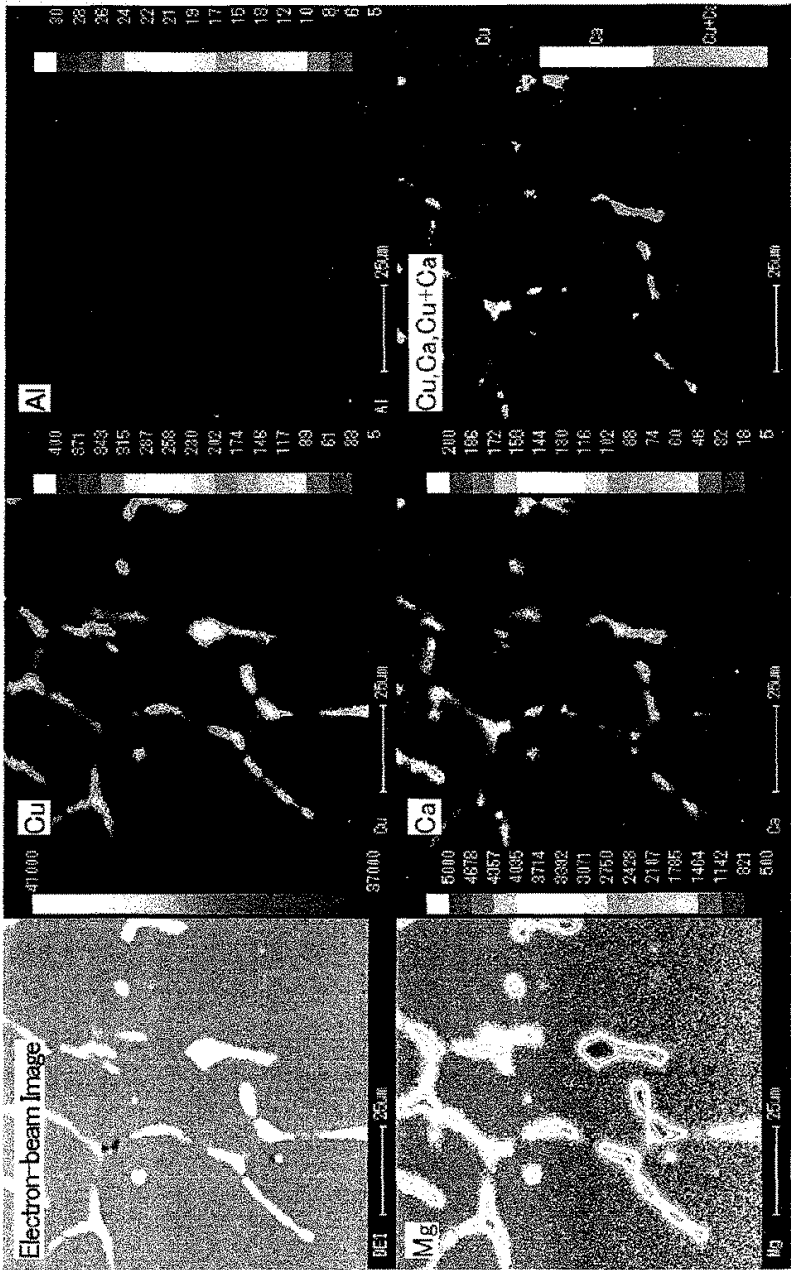(2006.01)i, *F02F1/00*(2006.01)i, *F02F1/24*(2006.01)i, *F04D29/02*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C23/00-C22C23/06, C22F1/06, F02B39/00, F02F1/00, F02F1/24, F04D29/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho   1922-1996   Jitsuyo Shinan Toroku Koho   1996-2008
Kokai Jitsuyo Shinan Koho   1971-2008   Toroku Jitsuyo Shinan Koho   1994-2008

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 7-11374 A (Ube Industries, Ltd., Nissan Motor Co., Ltd.), 13 January, 1995 (13.01.95), Claims; Par. Nos. [0001], [0015], [0027]; tables 3, 6 & US 5681403 A & GB 2296256 A	1-15
A	JP 6-25790 A (Mitsui Mining & Smelting Co., Ltd., Metallgesellschaft AG.), 01 February, 1994 (01.02.94), Claims; Par. Nos. [0001], [0016] (Family: none)	1-15

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 January, 2008 (28.01.08)	05 February, 2008 (05.02.08)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

33

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2005054233 A [0003]

Espacenet

Bibliographic data: CN101381829 (A) — 2009-03-11

Method for preparing in-situ particle reinforced magnesium base compound material

Inventor(s):	YUTAO ZHAO [CN]; GANG CHEN [CN]; YUNLONG XU [CN]; SONGLI ZHANG [CN] ± (ZHAO YUTAO, ; CHEN GANG, ; XU YUNLONG, ; ZHANG SONGLI)
Applicant(s):	UNIV JIANGSU [CN] ± (JIANGSU UNIVERSITY)
Classification:	- international: *C22C1/00; C22C23/00* - cooperative:
Application number:	CN20081155895 20081017
Priority number(s):	CN20081155895 20081017
Also published as:	CN101381829 (B)

Abstract of CN101381829 (A)

The invention relates to a method for preparing in-situ particle reinforced magnesia-based composite materials, which particularly comprises the following steps: magnesium aluminum alloy raw materials are completely smelt under the protective condition of gas mixture of SF6 and CO2; aluminum-silicon intermediate alloy is pressed into a magnesium aluminum fused mass, and the temperature is raised and maintained, so as to guarantee complete reaction between silicon and magnesium in the magnesium aluminum alloy fused mass, and simultaneously an ultrasonic probe is inserted into the fused mass for treatment; and after the treatment is finished, surface scum is removed and the fused mass is cast into a metal die, and the in-situ Mg2Si particle reinforced magnesia-based composite materials are obtained. The method has the characteristics of good interference compatibility of Mg2Si particles and substrates, controllable particle size of reinforced phases, uniform distribution of the reinforced phase and so on; and the magnesia-based composite materials prepared have good mechanical property.

[54] 发明名称
一种原位颗粒增强镁基复合材料的制备方法

[57] 摘要

本发明涉及一种原位颗粒增强镁基复合材料的制备方法，具体是：在 SF_6 和 CO_2 混合气体保护条件下，将镁铝合金原材料完全熔化；然后把 Al－Si 中间合金压入镁铝熔体中，升温并保温，以保证 Si 与镁铝合金熔体中的 Mg 完全反应，同时将超声探头插入熔体中进行处理；处理完成后升温，捞去表面的浮渣，并浇铸于金属模具中，得到原位 Mg_2Si 颗粒增强镁基复合材料。该方法具有 Mg_2Si 颗粒与基体的界面相容性好，增强相的颗粒尺寸可控，增强相分布均匀等特点，制备的镁基复合材料具有良好的力学性能。
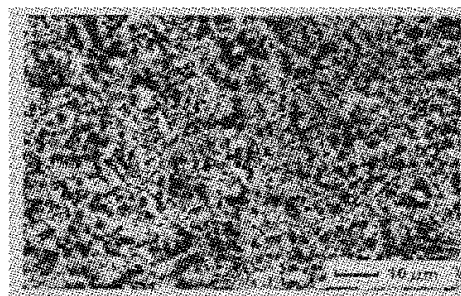
1、一种原位颗粒增强镁基复合材料的制备方法，其特征在于，包括以下步骤：

（1）在 SF_6 和 CO_2 混合气体保护条件下，将镁铝合金原材料完全熔化；

（2）然后把 Al-Si 中间合金压入镁铝熔体中，升温并保温，以保证 Si 与镁铝合金熔体中的 Mg 完全反应，同时将超声探头插入熔体中进行处理；

（3）处理完成后，去除表面的浮渣，并浇铸于金属模具中，得到原位 Mg_2Si 颗粒增强镁基复合材料。

2、根据权利要求 1 所述的原位颗粒增强镁基复合材料的制备方法，其特征在于，步骤（2）中，所述的升温，其温度升至 700~740℃。

3、根据权利要求 1 所述的原位颗粒增强镁基复合材料的制备方法，其特征在于，步骤（2）中，所述的保温，其时间为 10~20 分钟。

4、根据权利要求 1 所述的原位颗粒增强镁基复合材料的制备方法，其特征在于，步骤（2）中，所述的超声处理，其功率控制在 0.4~2.0KW。

5、根据权利要求 1 所述的原位颗粒增强镁基复合材料的制备方法，其特征在于，步骤（2）中，所述的超声处理，其处理时间为 5~15 分钟，处理方式为连续处理。

一种原位颗粒增强镁基复合材料的制备方法

技术领域

　　本发明涉及一种原位颗粒增强镁基复合材料的制备方法,特别是一种采用超声化学法制备原位颗粒增强镁基复合材料的方法。

背景技术

　　近年来,由于对环境、能源等问题的关注,镁基复合材料研究成为材料领域的热点。镁基复合材料具有高的比强度、比刚度,良好的铸造性和尺寸稳定性,抗电磁干扰及屏蔽性好,有良好的阻尼性能,减振性能好,对环境影响小,无污染,其废料回收利用率高达 85 %,因此在航天航空、汽车、计算机、网络、通讯等领域有广泛的应用前景。目前制备镁基复合材料主要是应用外加颗粒或纤维来增强。但是外加增强颗粒制备的复合材料中增强相的粒度大,颗粒与基体的润湿性较差,复合材料力学性能比较差;纤维增强的复合材料制备工艺复杂,成本比较高,在实际生产应用中受到限制。原位制备复合材料是近年来发展起来的制备方法,它具有制备的增强颗粒粒度细小,界面结合好,材料综合性能高的特点,在制备铝基复合材料方面取得了比较多的成功。

　　经对现有技术的文献检索发现,镁基复合材料的制备方法已经有不少文献报道,如中国专利号:CN101148722,名称为:"原位自生氮化铝和镁二硅增强镁基复合材料及其制备方法"。该专利的技术特点在于通过将搅拌铸造法和原位反应法结合起来,制备轻质、高强、高弹性模量的镁基复合材料。但是,仅仅利用搅拌熔体的方法不能细化增强相,同时增强相在基体中的分布也不均匀,所以这种制备方法具有一定的局限性。

发明内容

　　本发明的目的是针对现有技术的不足,提供一种原位颗粒增强镁基复合材料的制备方法。在制备过程中利用超声波作用于熔体,利用声空化和声流所引发的

力学效应中的搅拌、分散、除气、冲击破坏、疲劳损坏作用以及热学效应中整体加热、边界处的局部加热作用，细化复合材料的铸态组织，提高复合材料的力学性能。

本发明是通过以下技术方案实现的，将 Al-Si 中间合金加入到熔融的镁合金中，然后利用高能超声作用于熔体，最后将熔体静置后浇注成型。

本发明所涉及的原位颗粒增强镁基复合材料的制备方法，包含以下步骤：

（1）在 SF_6 和 CO_2 混合气体保护条件下，将镁铝合金原材料完全熔化；

（2）然后把 Al-Si 中间合金压入镁铝熔体中，升温并保温，以保证 Si 与镁铝合金熔体中的 Mg 完全反应，同时将超声探头插入熔体中进行处理；

（3）处理完成后，去除表面的浮渣，并浇铸于金属模具中，得到原位 Mg_2Si 自生颗粒增强镁基复合材料。

步骤（1）中，所述的熔化，其温度控制在 680~720℃。

步骤（1）中，所述的 SF_6 和 CO_2 混合气体，其中 SF_6 体积占 1~3%，CO_2 为余量。

步骤（2）中，所述的升温，其温度升至 700~740℃。

步骤（2）中，所述的保温，其时间为 10~20 分钟。

步骤（2）中，所述的超声处理，其功率控制在 0.4~2.0KW。

步骤（2）中，所述的超声处理，其处理时间为 5~15 分钟，处理方式为连续处理。

本发明的有益效果体现在：本发明以 AZ91 镁合金和 Al-Si 合金为原材料，采用高能超声和原位反应相结合的方法，成功制备了 Mg_2Si 颗粒增强镁基复合材料。由于 Mg_2Si 颗粒是在超声处理过程中通过化学反应在镁合金基体内原位生成的，与基体的界面相容性好，增强相的颗粒尺寸可控，增强相分布均匀等特点，因而制备的镁基复合材料具有良好的力学和物理性能；有效地避免了传统外加法制备复合材料时增强相的尺寸受限、增强相与基体结合不好、增强相分布不均匀等问题；超声化学方法的采用，还使为 Mg_2Si 相由原来的汉字状和尖角状转变成了颗粒状，同时颗粒的尺寸得到了细化，为制备镁基复合材料开辟了一条新的途径。

附图说明

图1是实施例1的Mg_2Si颗粒增强镁基复合材料的组织照片

具体实施方式

　　本发明的实施例以本发明技术方案为前提进行实施，给出了详细的实施方式和具体的操作过程，但本发明的保护范围不限于下述的实施例。

　　实施例1

　　在3vol.% SF_6+97vol.% CO_2混合气体保护的条件下，将AZ91D合金锭（80wt.%）在680℃完全熔化，然后把Al-Si中间合金（20wt.%）压入熔体中，接着将温度升高到700℃，并保温20分钟，将超声探头插入熔体中进行处理，超声功率设定为2KW，连续处理5分钟。最后去除表面的浮渣后浇铸于金属模具中凝固后得到11vol%Mg_2Si/AZ91D复合材料。所得原位Mg_2Si颗粒增强镁基复合材料的组织照片如图1，其室温拉伸强度为230MPa，150℃拉伸强度为202MPa。

　　实施例2

　　在2vol.% SF_6+98vol.% CO_2混合气体保护的条件下，将AZ91D合金锭（85wt.%）在700℃完全熔化，然后把Al-Si中间合金（15wt.%）压入熔体中，接着将温度升高到720℃，并保温15分钟，将超声探头插入熔体中进行处理，超声功率设定为1.6KW，连续处理8分钟。最后去除表面的浮渣后浇铸于金属模具中凝固后得到8 vol%Mg_2Si/AZ91D复合材料，所得Mg_2Si颗粒增强镁基复合材料的室温拉伸强度为：215MPa，150℃拉伸强度为188MPa。

　　实施例3

　　在1vol.% SF_6+99vol.% CO_2混合气体保护的条件下，将AZ91D合金锭（90wt.%）在720℃完全熔化，然后把Al-Si中间合金（10wt.%）压入熔体中，接着将温度升高到740℃，并保温10分钟，将超声探头插入熔体中进行处理，超声功率设定为0.4KW，连续处理15分钟。最后去除表面的浮渣后浇铸于金属模具中凝固后得到5vol%Mg_2Si/AZ91D复合材料，所得Mg_2Si颗粒增强镁基复合材料的室温拉伸强度为208MPa，150℃拉伸强度为175MPa。

图 1

Espacenet

Bibliographic data: CN102517489 (A) — 2012-06-27

Method for preparing Mg2Si/Mg composites by recovered silicon powder

Inventor(s):	PING GAO; CHUNXIA YANG; SHILEI DI; WENBO ZHANG; YONGLIANG GUO; JIANHUI DI; JIANHUA ZHANG; JINJUN LI; QIANG WANG $\pm$ (GAO PING, ; YANG CHUNXIA, ; DI SHILEI, ; ZHANG WENBO, ; GUO YONGLIANG, ; DI JIANHUI, ; ZHANG JIANHUA, ; LI JINJUN, ; WANG QIANG)
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Classification:	- international: *C22C1/02; C22C23/00; C22C32/00* - cooperative:
Application number:	CN20111451683 20111220 Global Dossier
Priority number(s):	CN20111451683 20111220
Also published as:	CN102517489 (B)

Abstract of CN102517489 (A)

The invention relates to a method for preparing Mg2Si/Mg composites by recovered silicon powder, which is characterized by including steps of drying a crucible required by experiment into a drying oven, adding magnesium alloy into a pit furnace for heating, injecting SF6+CO2 mixed protection gas and heating to the temperature ranging from 750 DEG C to 1100 DEG C for 1 to 3 hours until the magnesium alloy is melted; adding industrial dust silicon powder with 70% to 75% of silicon dioxide into water, adding the silicon powder, which is 2.5-7.5wt% of the magnesium alloy and wrapped by aluminum foil, into the magnesium alloy melt, ; mixing so that the magnesium alloy and the silicon powder can be reacted sufficiently; modifying, cooling naturally, then pouring the melt to a preheated metal mold with the preheating temperature ranging from 100 DEG C to 400 DEG C.; During the integral mixing and casting process, protection gas must be injected continuously, and accordingly the

Mg2Si/Mg composites are prepared. The industrial dust silicon powder is used as a silicon source and in-situ chemical reaction of the magnesium and the silicon powder is realized by means of mixing and casting. Themethod for preparing Mg2Si/Mg composites is simple in process and low in preparation cost, and the prepared Mg2Si/Mg composites are excellent in performances.
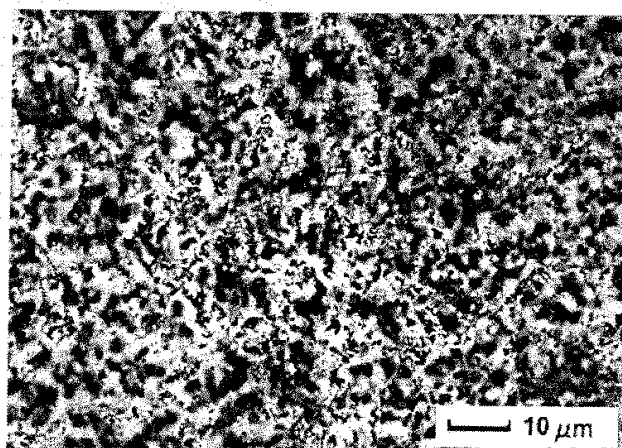
Espacenet

Bibliographic data: CN102517489 (A) — 2012-06-27

Method for preparing Mg2Si/Mg composites by recovered silicon powder

Inventor(s):	PING GAO; CHUNXIA YANG; SHILEI DI; WENBO ZHANG; YONGLIANG GUO; JIANHUI DI; JIANHUA ZHANG; JINJUN LI; QIANG WANG ± (GAO PING, ; YANG CHUNXIA, ; DI SHILEI, ; ZHANG WENBO, ; GUO YONGLIANG, ; DI JIANHUI, ; ZHANG JIANHUA, ; LI JINJUN, ; WANG QIANG)
Applicant(s):	INNER MONGOLIA WUER SPECIAL MATERIAL ENGINEERING TECHNOLOGY RES CT ± (INNER MONGOLIA WUER SPECIAL MATERIAL ENGINEERING TECHNOLOGY RESEARCH CENTER)
Classification:	- international: *C22C1/02; C22C23/00; C22C32/00* - cooperative:
Application number:	CN20111451683 20111220 Global Dossier
Priority number(s):	CN20111451683 20111220
Also published as:	CN102517489 (B)

Abstract of CN102517489 (A)

The invention relates to a method for preparing Mg2Si/Mg composites by recovered silicon powder, which is characterized by including steps of drying a crucible required by experiment into a drying oven, adding magnesium alloy into a pit furnace for heating, injecting SF6+CO2 mixed protection gas and heating to the temperature ranging from 750 DEG C to 1100 DEG C for 1 to 3 hours until the magnesium alloy is melted; adding industrial dust silicon powder with 70% to 75% of silicon dioxide into water, adding the silicon powder, which is 2.5-7.5wt% of the magnesium alloy and wrapped by aluminum foil, into the magnesium alloy melt, ; mixing so that the magnesium alloy and the silicon powder can be reacted sufficiently; modifying, cooling naturally, then pouring the melt to a preheated metal mold with the preheating temperature ranging from 100 DEG C to 400 DEG C.; During the integral mixing and casting process, protection gas must be injected continuously, and accordingly the

Mg2Si/Mg composites are prepared. The industrial dust silicon powder is used as a silicon source and in-situ chemical reaction of the magnesium and the silicon powder is realized by means of mixing and casting. Themethod for preparing Mg2Si/Mg composites is simple in process and low in preparation cost, and the prepared Mg2Si/Mg composites are excellent in performances.

(19) 中华人民共和国国家知识产权局

(12) 发明专利申请

(54) 发明名称

一种利用回收的硅粉制备 Mg₂Si/Mg 复合材料
的方法

(57) 摘要

本发明一种利用回收的硅粉制备 Mg₂Si/Mg
复合材料的方法,其特征是:将实验所需的坩埚
放入烘箱中烘干,镁合金放入井式炉中加热,同
时通入 SF_6+CO_2 混合的气体保护,加热 1～3 小
时至 750℃～1100℃ 使镁合金熔化,二氧化硅含
量为 70～75% 工业粉尘硅粉放入水中硅粉用
铝箔包裹加入,加入硅粉的重量百分比占镁合金
重量.25%～5.75%;搅拌,使镁合金和硅粉充
分反应;进行变质处理、自然降温,将熔体浇于预
热的金属型中,预热温度 100℃～400℃,在整个
搅拌铸造过程中,须持续通保护气体,即得本发
明 Mg₂Si/Mg 复合材料,本发明采用工业粉尘硅粉
作为硅源,通过搅拌铸造法实现镁和硅粉的原位
化学反应,工艺方法简单,制备成本低,制备出的
Mg₂Si/Mg 复合材料性能优良的。

CN 102517489 A

ECOMETAL-002303

1. 一种利用回收的硅粉制备 Mg_2Si/Mg 复合材料的方法,其特征是:

(a)、将实验所需的坩埚放入烘箱中烘干,烘箱的温度设置为 100℃～400℃;

(b)、将 300～420g 镁合金 AZ91D 放入井式炉中加热,同时通入 SF_6+CO_2 混合的气体保护,其中 10% 的 SF_6 和 90% 的 CO_2,加热 1～3 小时至 750℃～1100℃ 使镁合金熔化,用钢勺刮除表面杂质;

(c) 将二氧化硅的含量为 70%～75% 工业粉尘硅粉放入水中,除去水表面的漂浮物,然后滤去水,放入烘干箱中,温度设定为 70～85℃,烘干,硅粉用铝箔包裹加入步骤 (b) 中熔化的镁合金熔体中,加入的硅粉重量百分比为镁合金 AZ91D2 重量的 2.5%～5.75%,搅拌 10～60min,搅拌速度 400rpm～900rpm,使镁合金和硅粉充分反应;

(d)、变质处理:将 0.4wt%～2wt% Sb 元素用铝箔包裹后,用钟罩压入上述步骤 (c) 熔体中,搅拌 5min～40min;

(e)、自然降温:在降温过程中继续搅拌,冷却到 650℃～800℃,停止搅拌,将步骤 (d) 中的熔体浇于预热的金属型中,金属型的预热温度 100℃～400℃,在整个搅拌铸造过程中,须持续通保护气体,防止镁暴露在空气中氧化,熔体在金属型中自然冷却到室温,即得到本发明的 Mg_2Si/Mg 复合材料,Mg_2Si/Mg 复合材料中各成分的重量百分比含量为:Mg_2Si:3.50%～5.75%,MgO4.15%～6.45%,余量为 87.80%～92.35% 为 AZ91 镁合金;

(f)、热处理:将制备步骤 (e) 制备成的复合材料进行 T6 处理,以获得更高的性能,T6 处理工艺为:400～440℃保温 20～25h,然后淬入 20～30℃水中,最后在 200～250℃时效 4～8h。

一种利用回收的硅粉制备 Mg₂Si/Mg 复合材料的方法

技术领域

[0001] 本发明属于材料制备技术领域,涉及硅粉综合利用制备 Mg₂Si/Mg 复合材料。

背景技术

[0002] 钢铁和原镁生产中需要大量使用硅铁,生产硅铁产生的粉尘行业上称为硅粉,主要成分是二氧化硅,被认为是一种工业废弃物,严重污染了环境,因而硅粉的回收以及资源化利用具有十分重要的意义,硅粉中的二氧化硅属于无定形物质,活性高、颗粒细小、比表面积大,具有优良的理化性能,因而世界上许多国家对硅粉的再利用进行了大量的研究。早在 1947 年挪威埃肯公司 (ElkemASA) 就开始进行微硅粉的生产技术、粉尘处理、分级和应用方面的研究,成为世界上最早开展微硅粉研发的企业,并始终在微硅粉收尘与处理技术上保持领先地位。之后,美国、俄罗斯、日本也开始进行研发应用,并成为微硅粉主要生产国。目前,硅粉年生产量为:美国 30 万 t,俄罗斯 7 万 t,挪威 12 万 t,日本 7 万 t。美国、俄罗斯、挪威等国均有微硅粉造球专利和制球设备。

[0003] 我国对微硅粉的应用研究和回收利用起步较晚,近几年,由于国家对环保的重视,逐步加强了对污染企业的管理,特别是国内对高强混凝土需求的增加,许多铁合金生产企业配备了收尘设备,并开发、引进了加密技术。我国微硅粉产品发展迅速,在该领域与国外的差距逐步缩小。迫于节能减排的压力,汽车行业对镁合金的需求日趋迫切。由于镁合金存在强度不高(特别是高温强度)、刚度不足等弱点,目前镁合金主要应用于非结构件和非耐热件上,这极大地限制了镁合金在汽车行业的应用。由于含有高刚度和高强度的第二相颗粒,镁基复合材料具有高的刚度、良好的高温强度和抗蠕变能力,是汽车发动机的理想材料。由于 Mg₂Si 具有高熔点(1087℃)、低密度(1.99g/cm³)、高硬度(HV460)、低热膨胀系数(7.5×10⁻⁶K⁻¹)和高弹性模量(120GPa)等优点,Mg₂Si 颗粒增强镁基复合材料密度与镁合金相当,但具有更高的刚度、强度和抗蠕变能力,是汽车发动机的首选材料之一。在制备 Mg₂Si 增强镁基复合材料中,普遍使用结晶硅作为硅源。结晶硅材料是全球最主要的光伏材料,随着单晶硅和多晶硅在太阳能电池中广泛运用,硅原料紧缺的状况日益严重。成本是制约镁基复合材料在汽车上应用的最大障碍之一,在制备 Mg₂Si 增强镁基复合材料中如能用硅粉代替结晶硅,不仅可以实现硅粉的资源化利用,而且节约了日益昂贵的硅资源,具有重要的环保、资源和经济价值。

[0004] 硅粉的回收以及资源化利用是国家大力扶持和提倡的项目。对硅粉的资源化利用目前还处于初级阶段,如何高附加值地利用硅粉是硅粉资源化利用的主要技术难点。

[0005] Mg₂Si 增强镁基复合材料是汽车发动机的首选材料之一,目前面临的主要技术难点有二:(1)Mg₂Si 增强镁基复合材料成本高:如何降低 Mg₂Si 增强镁基复合材料的成本是制约其应用的关键之一。(2)Mg₂Si 增强镁基复合材料高温性能的最大化:Mg₂Si 的形态和分布控制以及尺度的细化,细小均匀分布圆形的 Mg₂Si 可以最大化 Mg₂Si 增强镁基复合材料的高温强度和蠕变抗力。

发明内容：

[0006]　　本发明的目的是针对上述技术难点,利用回收的硅粉与镁合金进行反应,通过搅拌铸造的方法制备低成本高性能 Mg_2Si 增强镁基复合材料。硅粉颗粒和其中的杂质相可以起到异质形核中心的作用,在优化工艺下,实现对 Mg_2Si 的形态、分布和尺度的控制,从而达到优良的高温强度和蠕变抗力;利用工业粉尘硅粉作为反应剂,大幅度降低复合材料的制造成本的一种利用回收的硅粉制备 Mg_2Si/Mg 复合材料的方法。

[0007]　　本发明的目的是这样实现的：

[0008]　　本发明采用工业粉尘硅粉作为硅源,通过搅拌铸造法实现镁和硅粉的原位化学反应,制备出了性能优良的 Mg_2Si/Mg 复合材料。

[0009]　　镁合金为 AZ 系列的镁合金,硅粉为工业粉尘硅粉,其中二氧化硅的含量为 70%～75%,复合材料制备是在井式电阻炉中进行,采用 SF_6+CO_2 混合的气体保护,其中 10% 的 SF_6 和 90% 的 CO_2,坩埚为钢制坩埚。

[0010]　　本发明一种利用回收的硅粉制备 Mg_2Si/Mg 复合材料的方法,其特征是：

[0011]　　(a)、将实验所需的坩埚放入烘箱中烘干,烘箱的温度设置为 100℃～400℃ ;

[0012]　　(b)、将 300～420g 镁合金 AZ91D 放入井式炉中加热,同时通入 SF_6+CO_2 混合的气体保护,其中 10% 的 SF_6 和 90% 的 CO_2,加热 1～3 小时至 750℃～1100℃ 使镁合金熔化,用钢勺刮除表面杂质;

[0013]　　(c) 将二氧化硅的含量为 70%～75% 工业粉尘硅粉放入水中,除去水表面的漂浮物,然后滤去水,放入烘干箱中,温度设定为 70～85℃,烘干,硅粉用铝箔包裹加入步骤 (b) 中熔化的镁合金熔体中,加入的硅粉重量百分比为镁合金 AZ91D2 重量的 2.5%～5.75%,搅拌 10～60min,搅拌速度 400rpm～900rpm,使镁合金和硅粉充分反应;

[0014]　　(d)、变质处理 :将 0.4wt%～2wt% Sb 元素用铝箔包裹后,用钟罩压入上述步骤 (c) 熔体中,搅拌 5min～40min;

[0015]　　(e)、自然降温 :在降温过程中继续搅拌,冷却到 650℃～800℃,停止搅拌,将步骤 (d) 中的熔体浇于预热的金属型中,金属型的预热温度 100℃～400℃,在整个搅拌铸造过程中,须持续通保护气体,防止镁暴露在空气中氧化,熔体在金属型中自然冷却到室温,即得到本发明的 Mg_2Si/Mg 复合材料,Mg_2Si/Mg 复合材料中各成分的重量百分比含量为 :Mg_2Si :3.50%～5.75%,Mg04.15%～6.45%,余量为 87.80%～92.35% AZ91 镁合金;

[0016]　　(f)、热处理 :将制备步骤 (e) 制备好的 Mg_2Si/Mg 复合材料进行 T6 处理,以获得更高的性能,T6 处理工艺为 :400～440℃ 保温 20～25h,然后淬入 20～30℃ 水中,最后在 200～250℃ 时效 4～8h。

[0017]　　利用本发明的方法制备的 Mg_2Si/Mg 复合材料优点如下：

[0018]　　(1) 利用了废弃的硅粉,一方面有利于环境保护,另一方面提升了废弃硅粉的再利用价值;

[0019]　　(2) 制备的 Mg_2Si/Mg 复合材料性能特点是轻质高强,具有较高的弹性模量 :55.18GPa 而镁合金仅为 44.8GPa ;而且强度达到了同类复合材料的上限水平;

[0020]　　(3) 该复合材料比镁合金具有更好的耐磨性;

[0021]　　(4) 应用领域主要航空航天等需要轻质高强性能和耐磨性能的领域;

[0022]　　(5) 制备方法简单。

具体实施方式

[0023] 实施例 1：

[0024] 镁合金为 AZ91D 镁合金,硅粉为工业粉尘硅粉,其中二氧化硅的含量为 70%,复合材料制备是在井式电阻炉中进行,采用 SF_6+CO_2 混合的气体保护,其中 10% 的 SF_6 和 90% 的 CO_2,坩埚为钢制坩埚。

[0025] Mg_2Si/Mg 复合材料的制备方法如下：

[0026] (a)、将实验所需的坩埚放入烘箱中烘干,烘箱的温度设置为 400℃；

[0027] (b)、将 AZ91D 镁合金 340g 放入井式炉中加热,同时通入保护气体,加热 2.5 小时至 950℃ 使镁合金熔化,用钢勺刮除表面杂质；

[0028] (c)、工业粉尘硅粉放入水中,除去水表面的漂浮物,然后滤去水,放入温度 70℃ 烘干箱中烘干,将 11.05g 硅粉用铝箔包裹加入到镁合金熔体中,搅拌 20min,搅拌速度 400rpm,使镁合金和硅粉充分反应；

[0029] (d)、变质处理:将 3.51gSb 元素用铝箔包裹后,用钟罩压入上述步骤 (c) 的熔体中,搅拌 5min；

[0030] (e)、自然降温:在降温过程中继续搅拌,冷却到 650℃,停止搅拌,将步骤 (d) 中的熔体浇于预热的金属型中,预热预热温度 400℃,在整个搅拌铸造过程中,须持续通保护气体,防止镁暴露在空气中氧化,熔体在金属型中自然冷却到室温,即得到本发明的 Mg_2Si/Mg 复合材料,制备的 Mg_2Si/Mg 复合材料中各成分的重量百分比含量为:Mg_2Si:4.50%、MgO:5.15%、其余为 AZ91 镁合金；

[0031] (f)、热处理:将制备步骤 (e) 制备好的 Mg_2Si/Mg 复合材料进行 T6 处理,以获得更高的性能；T6 处理工艺为:400℃ 保温 22h,然后淬入 24℃ 水中,最后在 200℃ 时效 4h。

[0032] 实施例 2：

[0033] 镁合金为 AZ91D 镁合金,硅粉为工业粉尘硅粉,其中二氧化硅的含量为 72%,复合材料制备是在井式电阻炉中进行,采用 SF_6+CO_2 混合的气体保护,其中 10% 的 SF_6 和 90% 的 CO_2,坩埚为钢制坩埚。

[0034] Mg_2Si/Mg 复合材料的制备方法如下：

[0035] (a)、将实验所需的坩埚放入烘箱中烘干,烘箱的温度设置为 300℃；

[0036] (b)、将 AZ91D 镁合金 380g 放入井式炉中加热,同时通入保护气体,加热 2 小时至 850℃ 使镁合金熔化,用钢勺刮除表面杂质；

[0037] (c)、工业粉尘硅粉放入水中,除去水表面的漂浮物,然后滤去水,放入烘干箱中,温度 75℃ 烘干,将 18.66g 硅粉用铝箔包裹加入到镁合金熔体中,搅拌 40min,搅拌速度 900rpm,使镁合金和硅粉充分反应；

[0038] (d)、变质处理:将 5.98gSb 元素用铝箔包裹后,用钟罩压入熔体中,搅拌 15min；

[0039] (e)、自然降温,在降温过程中继续搅拌,冷却到 700℃,停止搅拌,将步骤 (d) 的熔体浇于预热的金属型中,预热温度 300℃,在整个搅拌铸造过程中,须持续通保护气体,防止镁暴露在空气中氧化,熔体在金属型中自然冷却到室温,即得到本发明的 Mg_2Si/Mg 复合材料,制备的复合材料中各成分的重量百分比为:Mg_2Si:5.25%、MgO:5.87%,其余为 AZ91 镁合金。

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[0040] (f)、热处理 :将制备步骤 (e) 制备好的 Mg_2Si/Mg 复合材料进行 T6 处理,以获得更高的性能;T6 处理工艺为 :410℃保温 23h,然后淬入 20℃水中,最后在 220℃时效 5h。

[0041] 实施例 3 :

[0042] 镁合金为 AZ91D 镁合金,硅粉为工业粉尘硅粉,其中二氧化硅的含量约 74%,复合材料制备是在井式电阻炉中进行,采用 SF_6+CO_2 混合的气体保护,其中 10% 的 SF_6 和 90% 的 CO_2,坩埚为钢制坩埚。

[0043] Mg_2Si/Mg 复合材料的制备方法如下 :

[0044] (a)、将实验所需的坩埚放入烘箱中烘干,烘箱的温度设置为 200℃ ;

[0045] (b)、将 AZ91D 镁合金 300g 放入井式炉中加热,同时通入保护气体,加热 1 小时至 750℃使镁合金熔化,用钢勺刮除表面杂质 ;

[0046] (c)、工业粉尘硅粉放入水中,除去水表面的漂浮物,然后滤去水,放入温度为 80℃ 的烘干箱中烘干,将 6.91g 硅粉用铝箔包裹加入到镁合金熔体中,搅拌 10min,搅拌速度 750rpm,使镁合金和硅粉充分反应 ;

[0047] (d) 变质处理 :将 1.23gSb 元素用铝箔包裹后,用钟罩压入熔体中,搅拌 25min ;

[0048] (e)、自然降温,在降温过程中继续搅拌,冷却到 750℃,停止搅拌,将熔体浇于预热温度为 200℃的预热金属型中,在整个搅拌铸造过程中,须持续通保护气体,防止镁暴露在空气中氧化,熔体在金属型中自然冷却到室温,即得到本发明的 Mg_2Si/Mg 复合材料,制备的复合材料中个成分的重量百分比含量为 :Mg_2Si :3.50%、MgO :4.15%、余量为 AZ91 镁合金 ;

[0049] (f)、热处理 :将制备步骤 (e) 制备好的 Mg_2Si/Mg 复合材料进行 T6 处理,以获得更高的性能,T6 处理工艺为 :420℃保温 20h,然后淬入 28℃水中,最后在 240℃时效 7h。

[0050] 实施例 4 :

[0051] 镁合金为 AZ91D 镁合金,硅粉为工业粉尘硅粉,其中二氧化硅的含量为 75%,复合材料制备是在井式电阻炉中进行,采用 SF_6+CO_2,10% 的 SF_6 和 90% 的 CO_2 气体保护,坩埚为钢制坩埚。

[0052] Mg_2Si/Mg 复合材料的制备方法如下 :

[0053] (a)、将实验所需的坩埚放入烘箱中烘干,烘箱的温度设置为 100℃ ;

[0054] (b)、将 AZ91D 镁合金 420g 放入井式炉中加热,同时通入保护气体,加热 3 小时至 1100℃使镁合金熔化,用钢勺刮除表面杂质 ;

[0055] (c)、工业粉尘硅粉放入水中,除去水表面的漂浮物,然后滤去水,放入温度 85℃ 为烘干箱中烘干,将 25.62g 硅粉用铝箔包裹加入到镁合金熔体中,搅拌 60min,搅拌速度 550rpm,使镁合金和硅粉充分反应 ;

[0056] (d)、变质处理 :将 8.91gSb 元素用铝箔包裹后,用钟罩压入熔体中,搅拌 40min ;

[0057] (e)、自然降温,在降温过程中继续搅拌,冷却到 800℃,停止搅拌,将熔体浇于预热的金属型中,预热温度 100℃,在整个搅拌铸造过程中,须经常通保护气体,防止镁暴露在空气中氧化,熔体在金属型中自然冷却到室温,即得到本发明的 Mg_2Si/Mg 复合材料,制备的复合材料中各成分的重量百分比含量为 :Mg_2Si :5.75%、MgO :6.45%、其余为 AZ91 镁合金 ;

[0058] (f)、热处理 :将制备步骤 (e) 制备好的 Mg_2Si/Mg 复合材料进行 T6 处理,以获得更高的性能;T6 处理工艺为 :440℃保温 25h,然后淬入 30℃水中,最后在 250℃时效 8h。

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Light and pressure-proof fast-decomposed cast magnesium alloy

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Applicant(s):	UNIV CENTRAL SOUTH ± (CENTRAL SOUTH UNIVERSITY)
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The invention discloses light and pressure-proof fast-decomposed cast magnesium alloy which can be used as a tripping ball material for a multi-stage sliding sleeve staged-fracturing technique. The light and pressure-proof fast-decomposed cast magnesium alloy is prepared from the following components: 13-25% of Al, 2-15% of Zn, 0.1-5% of Fe, 0.05-5% of Cu, 0.05-5% of Ni, 0-5% of Ag, 0.05-0.5% of Zr, 0.05-0.5% of Ti, and the balance of Mg. The preparation method comprises the following steps of: weighing the components according to the designed component ratio of the magnesium alloy; firstly, putting pure magnesium and pure aluminum into a smelting furnace, putting pure zinc and intermediate alloy of other components into magnesium-aluminum alloy melt after melting; refining, degassing, and stewing after warming to melt; then casting in a protective atmosphere. The light and pressure-proof fast-decomposed cast magnesium alloy is reasonable in component ratio, and simple in craft process; the light and pressure-proof fast-decomposed cast magnesium alloy can be obtained by controlling the ingredients of the alloy; the alloy decomposition performance exceeds that of the traditional cast magnesium alloy; the demands of the multi-stage sliding sleeve staged-fracturing technique on the decomposition performance of the tripping ball material can be met; industrialized application can be

achieved; application of the magnesium alloy in the field of exploitation of petroleum and gas is expanded.

(54) 发明名称
一种轻质耐压快速分解的铸造镁合金

(57) 摘要

一种轻质耐压快速分解的铸造镁合金,可用做多级滑套分段压裂技术用憋压球材料。所述合金由下述组份组成:Al:13～25%,Zn:2～15%,Fe:0.1～5%,Cu:0.05～5%,Ni:0.05～5%,Ag:0～5%,Zr:0.05～0.5%,Ti:0.05～0.5%,余量为Mg。制备方法为:按设计的镁合金组分配比,称取各组分,先将纯镁、纯铝放入熔炼炉中,熔化后再将纯锌以及其他组分的中间合金放入镁铝合金熔体中,升温熔化后,精炼除气、静置,然后在保护气氛下浇铸。本发明组分配比合理、工艺过程简单,通过调控合金的成分,获得轻质耐压快速分解的铸造镁合金。合金分解性能超过现有铸造镁合金,能满足多级滑套分段压裂技术对憋压球材料分解性能的要求。可实现工业化应用.拓展了镁合金在石油天然气开采领域的应用。

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1. 一种轻质耐压快速分解的铸造镁合金,主要包括以下重量百分比的组分：

Al :13 ～ 25%,

Zn :2 ～ 15%,

余量为 Mg,各组分重量百分之和为 100%。

2. 根据权利要求 1 所述的一种轻质耐压快速分解的铸造镁合金,还包括以下重量百分比的微量元素组分：

Fe： 0.1～5%

Cu： 0.05～5%

Ni： 0.05～5%

Zr： 0.05～0.5%

Ti： 0.05～0.5%；各组分重量百分之和为 100%。

3. 根据权利要求 2 所述的一种轻质耐压快速分解的铸造镁合金,还包含重量百分比为 0 ～ 5% 的微量元素 Ag,各组分重量百分之和为 100%。

4. 制备如权利要求 1-3 任意一项所述一种轻质耐压快速分解的铸造镁合金的方法,包括下述步骤：

按设计的轻质耐压快速分解的铸造镁合金组分配比,称取各组分,先将纯镁、纯铝放入熔炼炉中,熔化后再将纯锌以及微量元素组分的中间合金放入镁铝合金熔体中,升温熔化后,精炼除气、静置,然后在保护气氛下浇铸。

5. 根据权利要求 4 所述的方法,其特征在于 :纯镁、纯铝的熔化温度为 700 ～ 730℃。

6. 根据权利要求 4 所述的方法,其特征在于 :纯锌以及其他组分的中间合金的熔化温度为 740 ～ 780℃。

7. 根据权利要求 4 所述的方法,其特征在于 :精炼除气温度为 720 ～ 750℃,通入氩气或者用 C_2Cl_6 进行精炼除气处理。

8. 根据权利要求 4 所述的方法,其特征在于 :静置、浇铸温度为 700 ～ 720℃,浇铸保护气氛为氩气或 SF_6 与空气的混合气。

9. 根据权利要求 4 所述的方法,其特征在于 :所述微量元素组分的中间合金分别是 Al-Fe 中间合金、Al-Ni 中间合金、Al-Cu 中间合金、Al-Ag 中间合金、Al-Zr 中间合金、Al-Ti 中间合金,中间合金经烘烤干燥后加入镁铝合金熔体中。

10. 根据权利要求 9 所述的方法,其特征在于 :轻质耐压快速分解的铸造镁合金中,组分铝的含量由微量元素组分的中间合金中的铝含量与镁铝合金熔体中的铝含量构成。

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一种轻质耐压快速分解的铸造镁合金

技术领域

[0001]　　本发明公开了一种轻质耐压快速分解的铸造镁合金。可作为石油天然气开采用多级滑套分段压裂技术用憋压球材料。属于镁合金制备技术领域。

背景技术

[0002]　　页岩气是指赋存于富有机质泥页岩及其夹层中,以吸附或游离状态为主要存在方式的非常规天然气,成分以甲烷为主,是一种清洁、高效的能源资源。近几年,美国页岩气勘探开发技术突破,产量快速增长,对国际天然气市场及世界能源格局产生重大影响,世界主要资源国都加大了对页岩气的勘探开发力度。多级滑套分段压裂技术是近年来油气井工程技术领域发展起来的一项新型石油、天然气储层改造技术,主要应用与页岩气和低渗透储层的定向井、水平井的压裂增产改造。该项技术可根据地层地质状况与储层开发的需要,采用封隔器将水平井分隔成若干段,通过地面头球控制装置向井内依次投入直径由小到大的憋压球,逐级打开滑套,有针对性地对产层岩石进行压裂,形成石油、天然气流体裂缝通道,以扩大油气产层的泄油面积,提高油气采收率。在这项技术中,关键部位之一是憋压球。憋压球主要有两个功能,1)将滑套打开,以便对产层岩石进行压裂;2)将与压裂液体和压力隔离。待到所有岩石产层压裂结束后,需要对井内油管进行泄压,以便利于后期油气井的生产。以往的常规方法是利用低层压力作用下把憋压球反排出井口,或使用钻具将滑套球座及憋压球钻掉,这些方法的不足之处在于,受地层压力及现场施工压力的影响,可能导致憋压球发生卡位,反排不成功,下入钻具进行磨铣会延长施工周期,增加施工成本与风险。因此,研制一种能承受压裂施工高压、井底高温,并在井内流体环境下能自行分解的憋压球,可有效降低施工风险,提高施工效率。美国专利公布了一种可分解的多层包覆的核壳结构式复合材料制备方法(美国专利, US2011/0132143A1, 2011 年),该专利显示,通过在纳米级核体金属粉末(如镁、铝、锌、锰及其合金)颗粒的表面,采用化学镀的方法,镀上多层不同金属或金属氧化物纳米级壳层,如 Al、Ni、Al_2O_3 等,然后再把镀层后复合粉末进行烧结,获得具有一定分解性能的纳米复合材料,但该方法要求在活性比较高的纳米级镁、铝、锌、锰及其合金粉表面镀多层纳米级金属或金属氧化物,极大的增加了该材料的生产成本,无法进行工业化生产。而中国专利（专利号 201110328251.9）公布了"一种用于分段压裂投球滑套打开的新材料憋压球",尽管该专利制备的材料密度比较低,但该专利采用的是高分子材料制备憋压球,憋压球材料在高温腐蚀介质中不发生分解,导致在多级滑套分段压裂技术中必需使用钻具将憋压球钻掉,极大地增加了生产成本。

[0003]　　现有的铸造镁合金主要是以 Mg-Al-Zn 系镁合金为代表,其中以 AZ91D 镁合金的应用最为广泛,该合金的主要成分及其重量百分比是 Al8.3 ～ 9.7、Zn0.35 ～ 1.0、Mn0.15 ～ 0.5、余量为镁,合金的抗压缩强度低于 250MPa,分解速率极低($\leq 5 \times 10^{-4}$g. cm^2. h)（中国有色金属学报,2007,17 卷 2 期,p181）,无法满足多级滑套分段压裂技术中对憋压球材料的轻质耐压可分解性能要求。

[0004]　　为了降低生产成本,制备具有一定强度和可分解的轻质耐压快速分解的憋压球材

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料,本发明者提出通过优化合金成分设计,利用自制的含稀土元素的熔剂处理,采用熔炼铸造方法,制备轻质耐压可快速分解的铸造镁合金。轻质金属材料主要是指密度低于 4.5g/cm³ 的材料,包括铝及其合金、镁及其合金、钛及其合金、锂及其合金,我们在前期的研究中发现,铝及其合金、钛及其合金在 93℃ 的 3%KCl 溶液中的分解速率低于 1×10^{-5} g. cm⁻². h⁻¹,无法满足多级滑套分段压裂技术中对憋压球材料的分解性能要求(要求 93℃ 的 3%KCl 分解速率大于 0.02g. cm⁻². h⁻¹)。而锂及其合金由于活性高,易氧化,在大气环境下无法进行有效的安全制备。

[0005]　　因此,我们选用以镁作为研究基础,通过调控化学成分与制备工艺,采用工业化生产方法,制备轻质耐压快速分解的铸造镁合金,以满足多级滑套分段压裂技术中对憋压球材料的分解性能要求。

发明内容

[0006]　　本发明的目的旨在针对现有页岩气开采用的多级滑套分段压裂技术中所使用的憋压球材料的技术不足和缺陷,提出一种组分配比合理、生产工艺简单、可有效分解的铸造镁合金及其制备方法,使镁合金的分解性能超过现有的铸造镁合金。

[0007]　　本发明是通过以下技术方案实现的:

[0008]　　一种轻质耐压快速分解的铸造镁合金,主要包括以下重量百分比的组分:

[0009]　　Al :13 ～ 25%

[0010]　　Zn :2 ～ 15%

[0011]　　余量为 Mg。

[0012]　　一种轻质耐压快速分解的铸造镁合金,还包括以下重量百分比的微量元素组分:

[0013]　　Al :13 ～ 25%,

[0014]　　Zn :2 ～ 15%,

[0015]　　Fe :0.1 ～ 5%,

[0016]　　Cu :0.05 ～ 5%,

[0017]　　Ni :0.05 ～ 5%,

[0018]　　Ag :0 ～ 5%,

[0019]　　Zr :0.05 ～ 0.5%,

[0020]　　Ti :0.05 ～ 0.5%,余量为 Mg。

[0021]　　一种轻质耐压快速分解的铸造镁合金的制备方法,包括下述步骤:

[0022]　　按设计的轻质耐压快速分解的铸造镁合金组分配比,称取各组分,先将纯镁、纯铝放入熔炼炉中,升温至 700 ～ 730℃,熔化后再将纯锌以及微量元素组分的中间合金放入镁铝合金熔体中,升温至 740-780℃;熔化后,降温至 720 ～ 750℃时,通入氩气或者用 C₂Cl₆ 精炼剂进行除气处理;然后,降温至 700 ～ 720℃,静置,在氩气或 SF₆ 与空气的混合气体保护下浇铸。

[0023]　　本发明一种轻质耐压快速分解的铸造镁合金的制备方法,所述微量元素组分的中间合金分别是 Al-Fe 中间合金、Al-Ni 中间合金、Al-Cu 中间合金、Al-Ag 中间合金、Al-Zr 中间合金、Al-Ti 中间合金,中间合金经烘烤干燥后加入镁铝合金熔体中。

[0024]　　本发明一种轻质耐压快速分解的铸造镁合金的制备方法,所述轻质耐压快速分解

的铸造镁合金中,组分铝的含量由微量元素组分的中间合金中的铝含量与镁铝合金熔体中的铝含量构成。

[0025]　　与现有技术相比,本发明的优点在于:

[0026]　　本发明采用高铝含量(重量百分比 13 ～ 25%)和高锌(重量百分比 2 ～ 10%)的镁合金,并添加提高镁合金腐蚀性能的 Fe、Cu、Ni、Ag 元素,并同时添加提高耐压强度的晶粒细化剂 Zr、Ti 元素。其中添加高铝含量的目的在于使镁合金中晶界处产生大量的阴极相 β (Mg$_{17}$Al$_{12}$) 相与共晶相,而镁基体 α 相作为阳极相,从而使得镁合金的基体与晶界形成大量的微电池,加速镁合金的腐蚀分解,但铝的添加质量分数不能超过 25%,因为过多的添加铝降低了阳极相 α 相的体积分数,从而减少了镁合金中的微电池数量。在镁合金中添加高锌含量的目的在于提高镁合金的强度,但过多的添加锌则降低了镁合金中的阴极相 β (Mg$_{17}$Al$_{12}$) 相的体积分数。Fe、Cu、Ni、Ag 等元素在镁合金由于形成了大量金属间化微颗粒,能提高镁合金的腐蚀性能,从而能促进镁合金的分解。而微量 Zr、Ti 元素的添加可细化镁合金晶体,从而提高合金的耐压强度。本发明制备的轻质耐压快速分解铸造镁合金室温抗拉强度 σ$_b$ 比现有 AZ91D 镁合金提高 130 ～ 180MPa,于 70℃、3%KCl 溶液中的分解速率是现有 AZ91D 镁合金的 60-200 倍,于 93℃、3%KCl 溶液中的分解速率是现有 AZ91D 镁合金的 50-200 倍。

[0027]　　综上所述,本发明组分配比合理、生产工艺简单、可有效提高镁合金的总体强度和可分解性能。采用熔炼铸造方法,通过调控合金的成分与制备工艺,可获得轻质耐压快速分解的铸造镁合金,使其性能满足多级滑套分段压裂技术中憋压球材料的性能要求。从而拓展了镁合金在石油天然气开采领域的应用。形成可实际工业应用的铸造镁合金及其制备方法。

具体实施方式

[0028]　　根据本发明的特点,采用熔炼铸造方法,通过化学成分调控,获得室温压缩强度超过现有铸造的工业铸造镁合金,而在高温氯化钾溶液(70℃或者 93℃的质量分数为 3% 氯化钾水溶液)中的分解性能明显超过现有的铸锭冶金型镁合金 (如 Mg-Al-Zn 系的 AZ91D 镁合金)。具体实施例说明如下:

[0029]　　本发明实施例及对比例的合金组分配比见表 1,实施例及对比例制备的合金性能指标见表 2

[0030]　　对比例 1

[0031]　　对比合金为 AZ91D 镁合金,该合金的化学成分为:

[0032]　　Mg-9Al-1Zn-0.3Zr-0.1Mn(质量分数),合金配料(原料为:纯铝、纯镁、Al-4Zr 中间合金、Al-10Mn 中间合金、纯锌)在中频感应电阻炉中熔炼,并用 C$_2$Cl$_6$ 进行精炼处理,经过静置、扒渣,在氩气保护下通过铁模浇铸成坯锭。

[0033]　　实施例 1

[0034]　　合金的组份及其重量百分比为:

[0035]　　13%Al-2%Zn-0.1%Fe-5%Ni-2.5%Ag-0.5%Ti-0.5%Zr,其余为 Mg。

[0036]　　制备方法是:先将纯镁、纯铝放入熔炼炉中,升温至 700℃;熔化后再将经烘烤的 Al-Fe 中间合金、Al-Ni 中间合金、Al-Ag 中间合金、Al-Zr 中间合金、Al-Ti 中间合金及纯

锌放入镁铝合金熔体中,同时升温至 740℃;熔化后,降温至 720℃时,通入氩气进行除气处理;降温至 700℃,静置,在氩气保护下浇铸,冷却。

[0037] 实施例 2

[0038] 合金的组份及其重量百分比为:

[0039] 15%Al-5%Zn-0.5%Fe-0.1%Ni-0.1%Ti-0.1%Zr,其余为 Mg。

[0040] 制备方法是:先将纯镁、纯铝放入熔炼炉中,升温至 730℃;熔化后再将经烘烤的 Al-Fe 中间合金、Al-Ni 中间合金、Al-Zr 中间合金、Al-Ti 中间合金及纯锌放入镁铝合金熔体中,同时升温至 760℃;熔化后,降温至 730℃时,通入氩气进行除气处理;降温至 710℃,静置,在 SF₆ 与空气的混合气体保护下浇铸,冷却。

[0041] 实施例 3

[0042] 合金的组份及其重量百分比为:

[0043] 20%Al-10%Zn-5%Fe-2.5%Ni-2.5%Cu-5%Ag-0.25%Ti-0.25%Zr,其余为 Mg。

[0044] 制备方法是:先将纯镁、纯铝放入熔炼炉中,升温至 715℃;熔化后再将经烘烤的 Al-Fe 中间合金、Al-Ni 中间合金、Al-Cu 中间合金、Al-Ag 中间合金、Al-Zr 中间合金、Al-Ti 中间合金及纯锌放入镁铝合金熔体中,同时升温至 780℃;熔化后,降温至 750℃时,用氩气 与 C₂Cl₆ 精炼剂进行除气处理;降温至 700℃,静置,在氩气保护下浇铸,冷却。

[0045] 实施例 4

[0046] 合金的组份及其重量百分比为:

[0047] 18%Al-8%Zn-2.5%Fe-2.0%Ni-5%Cu-1%Ag-0.3%Ti-0.15%Zr,其余为 Mg。

[0048] 制备方法是:先将纯镁、纯铝放入熔炼炉中,升温至 715℃;熔化后再将经烘烤的 Al-Fe 中间合金、Al-Ni 中间合金、Al-Cu 中间合金、Al-Ag 中间合金、Al-Zr 中间合金、Al-Ti 中间合金及纯锌放入镁铝合金熔体中,同时升温至 750℃;熔化后,降温至 730℃时,用 C₂Cl₆ 精炼剂进行除气处理;降温至 710℃,静置,在氩气保护下浇铸,冷却。

[0049] 实施例 5

[0050] 合金的组份及其重量百分比为:

[0051] 20%Al-5%Zn-0.8%Fe-0.05%Ni-0.05%Cu-0.05%Ti-0.1%Zr,其余为 Mg。

[0052] 制备方法是:先将纯镁、纯铝放入熔炼炉中,升温至 730℃;熔化后再将经烘烤的 Al-Fe 中间合金、Al-Ni 中间合金、Al-Cu 中间合金、Al-Zr 中间合金、Al-Ti 中间合金及纯锌放入镁铝合金熔体中,同时并升温至 750℃;熔化后,降温至 730℃时,用氩气进行除气处理;降温至 720℃,静置,在氩气保护下浇铸,冷却。

[0053] 实施例 6

[0054] 合金的组份及其重量百分比为:

[0055] 15%Al-6%Zn-1.5%Fe-0.2%Ni-1%Cu-2%Ag-0.15%Ti-0.1%Zr,其余为 Mg。

[0056] 制备方法是:先将纯镁、纯铝放入熔炼炉中,升温至 720℃;熔化后再将经烘烤的 Al-Fe 中间合金、Al-Ni 中间合金、Al-Cu 中间合金、Al-Ag 中间合金、Al-Zr 中间合金、Al-Ti 中间合金及纯锌放入镁铝合金熔体中,同时升温至 770℃;熔化后,降温至 740℃时,用 C₂Cl₆ 精炼剂进行除气处理;降温至 700℃,静置,在 SF₆ 与空气的混合气体保护下浇铸,冷却。

[0057] 实施例 7

[0058] 合金的组份及其重量百分比为:

[0059]　　25%Al-10%Zn-1%Fe-0.5%Ni-0.1%Cu-0.5%Ti-0.05%Zr，其余为 Mg。

[0060]　　制备方法是：先将纯镁、纯铝放入熔炼炉中，升温至 730℃；熔化后再将经烘烤的
Al-Fe 中间合金、Al-Ni 中间合金、Al-Cu 中间合金、Al-Ag 中间合金、Al-Zr 中间合金、Al-Ti
中间合金及纯锌放入镁铝合金熔体中，同时升温至 760℃；熔化后，降温至 730℃时，，用氩气
与 C$_2$Cl$_6$ 精炼剂进行除气处理；降温至 710℃，静置，在氩气保护下浇铸，冷却。

[0061]　　表 1 本发明铸态合金的主要化学成分（重量百分比）

[0062]

合金	Al	Zn	Fe	Ni	Cu	Ag	Ti	Zr	Mn	Mg
对比例 1 (AZ91D)	9.00	1.00	0	0	0	0	0	0.01	0.03	余量
实施例 1	13	1.3	0.1	5	0	2.5	0.5	0.5	0	余量
实施例 2	15	5	0.5	0.1	0	0	0.1	0.1	0	余量
实施例 3	20	10	5	2.5	2.5	5	0.25	0.25	0	余量
实施例 4	18	8	2.5	2.0	5	1	0.3	0.15	0	余量
实施例 5	20	5	0.8	0.05	0.05	0	0.05	0.1	0	余量
实施例 6	15	6	1.5	0.2	1	2	0.15	0.1	0	余量
实施例 7	25	10	1	0.5	0.1	0	0	0.5	0.05	0	余量

[0063]　　表 2 本发明铸态合金室温压缩强度与高温分解速率

[0064]

	室温抗拉强度 σ$_b$ (MPa)	70℃在 3%KCl 溶液中的分解速率(g.cm^{-2}.h^{-1})	93℃在 3%KCl 溶液中的分解速率 (g.cm^{-2}.h^{-1})
对比例 1	232	0.00026	0.0005
实施例 1	360	0.035	0.074
实施例 2	385	0.015	0.045
实施例 3	410	0.013	0.036
实施例 4	375	0.034	0.058
实施例 5	392	0.025	0.048
实施例 6	365	0.021	0.063
实施例 7	387	0.036	0.057

[0065]　　比较实施例与对比例的性能参数值，可以看出：本发明制备的铸造镁合金的抗压
缩强度明显高于对比实施例合金，而在 70℃及 93℃在 3%KCl 溶液中的分解速率明显超过了
对比实施例合金，能满足多级滑套分段压裂技术中憋压球材料的轻质耐压快速分解的性能
要求。

Espacenet

Bibliographic data: CN102796928 (A) — 2012-11-28

High-performance magnesium base alloy material and method for preparing same

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Classification:	- international: $C22C23/06$; $C22F1/06$ - cooperative:
Application number:	CN20121324168 20120905 Global Dossier
Priority number(s):	CN20121324168 20120905
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Abstract of CN102796928 (A)

The invention discloses a high-performance magnesium base alloy material and a method for preparing the high-performance magnesium base alloy material, which are designed for achieving the purpose that a great quantity of small reinforcements which have good thermal stability and are generated when the form of magnesium base alloy is varied and small recrystallization macrostructures which are produced through the small reinforcements are obtained for improving the shear strength of the magnesium base alloy. Mg alloy is taken as a basic material, Er, Cu and Ag which improve the non-crystallizing forming capability of the Mg alloy are selected as alloying elements, and common casting and hot extrusion methods are selected for preparing the alloy material.; Because negative formation heat is generated among the elements and the atomic radiuses are more different from each other, a great quantity of interatomic solute clusters are firstly formed during the extrusion process, and furthermore, small intermetallic compound particles with stable mechanical property at high temperature can be separated out on the basis. Moreover, the macrostructure of the alloy is also thinned. The alloy can have very high strength and good plasticity within the range of

room temperature to 300 DEG C.

(54) 发明名称
一种高性能镁基合金材料及其制备方法

(57) 摘要

一种高性能镁基合金材料及其制备方法，是为了解决镁基合金在变形态下得到大量细小、热稳定好的增强体及由此得到细小的再结晶宏观组织，以提高镁合金服役性能的技术问题而设计的。本发明以 Mg 合金为基础，选择具有提高 Mg 合金非晶化形成能力的 (Er,Cu,Ag) 作为合金化元素，选用普通熔铸和热挤压方法制备该合金材料。由于元素之间具有负的生成热以及原子半径尺寸相差较大，在挤压过程中首先形成大量的原子间的束集 (solute clusters)，进而在此基础上析出细小的高温下力学性能稳定的金属间化合物粒子。同时，合金的宏观组织也得以细化。使得合金在室温至 300℃ 温度区间均具有很高的强度和很好的塑形。

CN 102796928 A
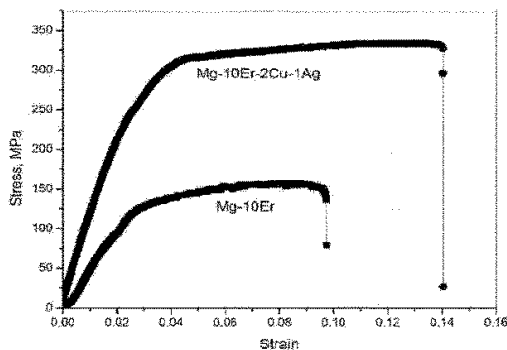
1. 一种高性能镁基合金材料,该材料以 Mg-Er 合金为基础,其特征在于:在所述 Mg-Er 中间合金的基础上,选择加入适量的 Cu,Ag 作为 Mg-Er 的合金化元素;其中:Er 的质量比 8-10%;Cu 的质量比 1-2%;Ag 的质量比 0.5-1%;余量,Mg。

2. 一种高性能镁基合金材料的制备方法,该方法中 Mg,Er,Cu,Ag 按上述质量配比,采用普通熔铸的方法,在 430℃下,以 5mm/min 慢速进行热挤压;在热挤压后续的空冷过程中,快速形成的大量的溶质元素的束集可作为异质形核质点析出细小热稳定优异的 $Mg_5(Er,Cu,Ag)$ 相增强体;同时,宏观组织得以细化;由此完成制备具有高服役性能的镁基合金的制备过程。

一种高性能镁基合金材料及其制备方法

技术领域：

[0001]　　　本发明涉及一种以镁合金为基础的材料及其制备方法，尤其涉及一种具有高性能的镁基合金材料及其制备方法。属于材料科学技术领域。

背景技术：

[0002]　　　发展高性能变形稀土镁合金一直是国内外学者的研究热点。目前研究思路集中在Mg-Gd 二元系通过添加多元强化合金元素（Zn，Ca，Zr，Y，Nd 等）以提高其力学性能。但目前开发的变形态 Mg-Gd 基稀土镁合金强度和塑性还有待进一步提高。而且目前开发的一般的变形 Mg-Gd 二元系基高性能镁合金随温度升高，强度下降很快，在接近 300°C 高温强度很低，只有几十 MPa，不能满足高温结构材料的服役要求。镁-钍系合金具有很高的耐热性，可用在 300°C 左右高温下工作的结构材料。但该合金系的室温强度低，生成工艺复杂，加上钍有放射性，对人体和环境的危害很大，因此可利用的价值不高。研究表明，如何在变形态下得到大量细小、热稳定好的的增强体，并由此得到细小的再结晶宏观组织是提高镁合金服役性能的关键。

发明内容：

[0003]　　　本发明针对现有变形镁合金材料存在的不足，为了解决在变形态下得到大量细小、热稳定好的增强体及由此得到细小的再结晶宏观组织，以提高镁合金服役性能的技术问题，提供了一种高性能镁基合金材料及其制备方法。

[0004]　　　所述镁基合金材料，以 Mg-Er 中间合金为基础，选择加入适量的具有提高 Mg 合金非晶形成能力的 Cu，Ag 作为 Mg-Er 的合金化元素。

[0005]　　　其中：Er 的质量比 8-10% ；Cu 的质量比 1-2% ；Ag 的质量比 0.5-1% ；余量，Mg。

[0006]　　　高性能镁基合金材料的制备方法，该方法中 Mg，Er，Cu，Ag 按上述质量配比，采用普通熔铸的方法，在 430℃下，以 5mm/min 慢速进行热挤压，在后续空冷的条件下，以快速形成大量的溶质元素的束集中作为异质形核的质点，析出细小热稳定优异的 Mg5(Er，Cu，Ag) 相增强体 ；同时，宏观组织得以细化。由此完成制备具有高服役性能的镁基合金的制备过程。

[0007]　　　本发明的特点及有益效果 ：本发明制备的是一种具有优异热稳定性的、细小金属间化合物粒子增强的、宏观组织细小的变形镁合金。在本发明中，由于元素之间具有负的生成热以及原子半径尺寸相差较大，在挤压及后续的空冷过程中，首先形成大量的原子间的束集（solute clusters），进而在此基础上析出细小的高温下力学性能稳定的金属间化合物粒子，成分为 Mg5(Er，Cu，Ag)。而在后续的再结晶过程中，由于析出粒子刺激形核机制（particles stimulated nucleation），使得再结晶晶粒变的相对细小。这种组织使得合金热挤压态合金在很宽的温度范围内（室温至 350°C）保持很高的拉伸力学性能。室温下抗拉强度要略高于目前国内开发的高性能变形镁合金，并且保持 15% 的良好的拉伸塑性。高温下力学性能均要高于镁-钍系合金，体现出该材料在高温下使用极具潜力。热挤压态

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Mg-Er-Cu-Ag 四元合金优异的力学性能来自于复合强韧化,包括细晶强韧化,以及热稳定极好的析出相强化。

[0008] 作为高强度高塑性耐热镁合金,本材料研发的应用领域主要着眼于航空领域,满足该领域对镁合金材料使用温度一般为 200°C 至 300°C 的要求。还可以将该系列镁合金加工成多种形式的产品,如棒材、板材、型材和锻件等,主要用做超音速飞机、火箭、导弹的蒙皮材料及结构件。另外,也可以应用在汽车、机器制造和电子等工业部门。

附图说明:

[0009] 图 1 热挤压态多元 Mg-Er-Cu-Ag 相与二元 Mg-Er 合金在室温下塑性和强度的比较

[0010] 图 2 热挤压态多元 Mg-Er-Cu-Ag 的透射电镜照片

具体实施方式:

[0011] 一种高性能镁基合金材料,该材料以 Mg-Er 合金为基础,在所述 Mg-Er 中间合金的基础上,选择加入适量的 Cu,Ag 作为 Mg-Er 的合金化元素;其中:Er 的质量比 8-10%;Cu 的质量比 1-2%;Ag 的质量比 0.5-1%;余量,Mg。

[0012] 所述高性能镁基合金材料的制备方法,该方法中 Mg,Er,Cu,Ag 按上述质量配比,采用普通熔铸的方法,在 430℃下,以 5mm/min 慢速进行热挤压,在后续空冷的条件下,以快速形成大量的溶质元素的束集中作为异质形核的质点,析出细小热稳定优异的 $Mg_5(Er, Cu, Ag)$ 相增强体;同时,宏观组织得以细化。由此完成制备具有高服役性能的镁基合金的制备过程。

[0013] 实施例 1

[0014] 采用纯 Mg-10Er 中间合金以及纯 Cu,Ag 元素,按 87Mg-10Er-2Cu-1Ag(质量比)进行配制合金元素。采用普通铸造的方法,在 760 度下熔炼,保温 20 分钟浇铸成直径为 50mm 的棒材。然后进行 450℃/24h 均匀化处理;再在 430℃下进行热挤压,挤压比 12:1,挤压速率 5mm/min。挤压所得棒材为空冷处理。热挤压态合金在很宽的温度范围内(室温至 350°C)保持很高的拉伸力学性能,在室温下抗拉强度为 373MPa,屈服强度为 232MPa,拉伸延伸率 14.5%。参看图 1,热挤压态多元 Mg-Er-Cu-Ag 相与二元 Mg-Er 合金在室温下塑性和强度的比较;图 2 为热挤压态多元 Mg-Er-Cu-Ag 的透射电镜照片。

[0015] 实施例 2

[0016] 采用纯 Mg-8Er 中间合金以及纯 Cu,Ag 元素,按 89Mg-8Er-2Cu-1Ag(质量比)进行配制合金元素。在 760 度下熔炼,保温 20 分钟浇铸成直径为 50mm 的棒材。然后进行 450℃/24h 均匀化处理。然后,在 430℃进行热挤压,挤压比 12:1,挤压速率 5mm/min。挤压所得棒材为空冷处理。热挤压态合金在很宽的温度范围内(室温至 350°C)保持很高的拉伸力学性能,在 300°C 下抗拉强度为 161MPa,屈服强度为 148.54MPa,拉伸延伸率 47%。

[0017] 实施例 3

[0018] 采用纯 Mg-8Er 中间合金以及纯 Cu,Ag 元素,按 90Mg-8Er-1Cu-1Ag(质量比)进行配制合金元素。在 760 度下熔炼,保温 20 分钟浇铸成直径为 50mm 的棒材。然后进行 450℃/24h 均匀化处理。然后,在 430℃进行热挤压,挤压比 12:1,挤压速率 5mm/min。挤压所得棒材为空冷处理。热挤压态合金在很宽的温度范围内(室温至 350°C)保持很高的拉

伸力学性能,350° C 下抗拉强度为 106MPa,屈服强度为 90MPa,拉伸延伸率 59.5%。

[0019]　　　实施例 4

[0020]　　　采用纯 Mg-8.5Er 中间合金以及纯 Cu,Ag 元素,按 89.5Mg-8.5Er-1.5Cu-0.5Ag(质量比)进行配制合金元素。在 760 度下熔炼,保温 20 分钟浇铸成直径为 50mm 的棒材。然后进行 450℃/24h 均匀化处理。然后,在 430℃进行热挤压,挤压比 12:1,挤压速率 5mm/min。挤压所得棒材为空冷处理。热挤压态合金在很宽的温度范围内(室温至 350° C)保持很高的拉伸力学性能,350° C 下抗拉强度为 110MPa,屈服强度为 90MPa,拉伸延伸率 61.3%。

[0021]　　　实施例 5

[0022]　　　采用纯 Mg-8Er 中间合金以及纯 Cu,Ag 元素,按 90.5Mg-8Er-1Cu-0.5Ag(质量比)进行配制合金元素。在 760 度下熔炼,保温 20 分钟浇铸成直径为 50mm 的棒材。然后进行 450℃/24h 均匀化处理。然后,在 430℃进行热挤压,挤压比 12:1,挤压速率 5mm/min。挤压所得棒材为空冷处理。热挤压态合金在很宽的温度范围内(室温至 350° C)保持很高的拉伸力学性能,350° C 下抗拉强度为 103MPa,屈服强度为 88MPa,拉伸延伸率 61%。

图 1

图 2

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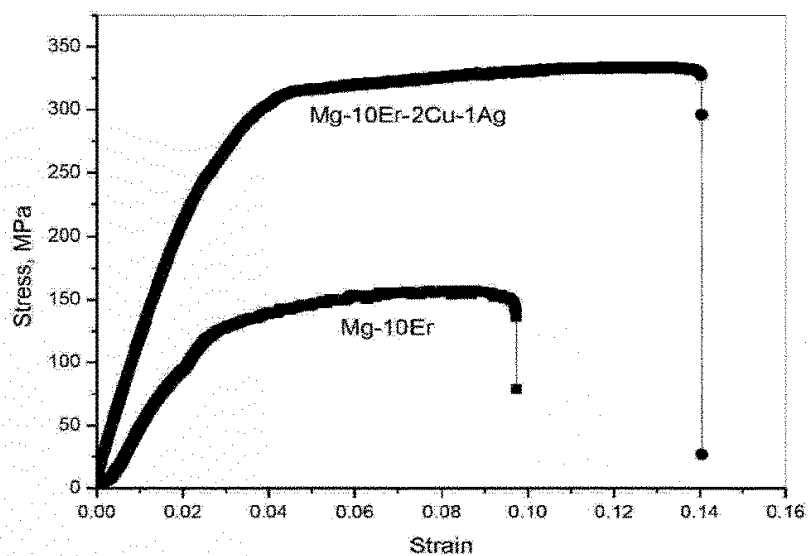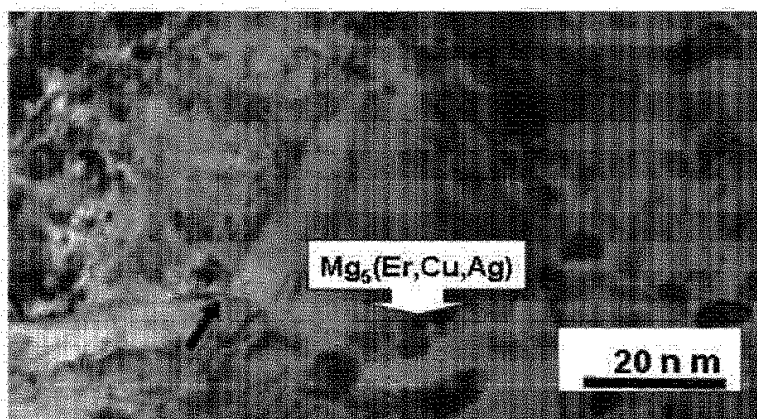
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EFS ID:	30419068
Application Number:	15641439
International Application Number:	
Confirmation Number:	2533
Title of Invention:	Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools
First Named Inventor/Applicant Name:	Brian P. Doud
Customer Number:	27885
Filer:	Brian Erkin Turung/mel rohan
Filer Authorized By:	Brian Erkin Turung
Attorney Docket Number:	POWD 200033US01
Receipt Date:	20-SEP-2017
Filing Date:	05-JUL-2017
Time Stamp:	12:37:24
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	no

File Listing:

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Warnings:

Information:

17	Foreign Reference	CN102796928.pdf	744135 66aa42b91411b8ff5425b6a0320ce7834dc bb1a0	no	8

Warnings:

Information:

18	Non Patent Literature	Sigworth.pdf	755753 f143b95f39bc14d3b39571f745a91a2cf921 2bd0	no	12

Warnings:

Information:

19	Non Patent Literature	Momentive.pdf	277872 064b34104f0481142fb8bac4203bd4dcb5e 76b91	no	2

Warnings:

Information:

20	Non Patent Literature	Durbin.pdf	1217004 aa53c23ef4a3fa3d1596bcb61fcbe5b16cfo 61cd	no	47

Warnings:

Information:

21	Non Patent Literature	Peguet.pdf	772517 070ea9494f3b888a44320d9541d3c7674fb 3470d	no	16

Warnings:

Information:

22	Non Patent Literature	ElementalCharts.pdf	791191 b29e263cc364aeaeff6ff8f8c29c99811ed65 9d7	no	9

Warnings:

Information:

| 23 | Non Patent Literature | Song.pdf | 4887409 | no | 23 |
| | | | b09c59ae626711225fbc161480229448b77 2a6b6 | | |

Warnings:

Information:

| 24 | Non Patent Literature | Zhou.pdf | 1212605 | no | 7 |
| | | | 2d6285c99b855a7921150e59ff4b9b951eff a0d4 | | |

Warnings:

Information:

| 25 | Non Patent Literature | Trojanova.pdf | 4591396 | no | 37 |
| | | | 98db671513401a31c1677e018e409330f90 dec3e | | |

Warnings:

Information:

| 26 | Non Patent Literature | SiliconCarbideNanoparticlesPro perties_Applications.pdf | 126559 | no | 2 |
| | | | 215f72172ed529508b5e908495268d5480f 6350f | | |

Warnings:

Information:

| 27 | Non Patent Literature | Magnesium_AZ91DF_Alloy.pdf | 134283 | no | 3 |
| | | | cda88445a40e15678c689ba6effe6d1576b9 4f1e | | |

Warnings:

Information:

| 28 | Non Patent Literature | Elasser.pdf | 3779987 | no | 19 |
| | | | 6f1200cb10cdbeb9f12f720638c917941cac 857a | | |

Warnings:

Information:

| 29 | Non Patent Literature | Lan.pdf | 1265315 | no | 7 |
| | | | 24f780b8e8d8d91eee6496a6530eabd7452 4644c | | |

Warnings:

Information:

| 30 | Non Patent Literature | Casati.pdf | 2379205 a71563f1585b188e36fad25facdf2fdb3d4f8 178 | no | 19 |

Warnings:

Information:

Total Files Size (in bytes):	47029098

This Acknowledgement Receipt evidences receipt on the noted date by the USPTO of the indicated documents, characterized by the applicant, and including page counts, where applicable. It serves as evidence of receipt similar to a Post Card, as described in MPEP 503.

<u>New Applications Under 35 U.S.C. 111</u>
If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
<u>National Stage of an International Application under 35 U.S.C. 371</u>
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
<u>New International Application Filed with the USPTO as a Receiving Office</u>
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

FIRST NAMED INVENTOR	:	Brian Doud
FOR	:	Galvanically-Active In Situ Formed Particles For Controlled Rate Dissolving Tools
SERIAL NO.	:	15/641,439
FILED	:	July 5, 2017
EXAMINER	:	
ART UNIT	:	1735
CONFIRMATION NO.	:	2533
ATTORNEY DOCKET NO.	:	POWD 200033US02

INFORMATION DISCLOSURE STATEMENT

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Dear Commissioner:

In accordance with 37 C.F.R. §§ 1.56, 1.97, 1.98 and MPEP §609, Applicant submits the following Information Disclosure Statement concerning information of which the Applicant is aware. Form PTO/SB/08a is submitted herewith.

This Information Disclosure Statement should not be construed to be an admission that any information referred to herein or submitted herewith is "prior art" or is considered to be material to patentability for this invention. No aspect of this submission constitutes a disclaimer of claim scope.

The United States Patent and Trademark Office OG Notice dated 12 October 2004 published a final rule revising 37 C.F.R. 1.98 dealing with the content of Disclosure Statements. Paragraph (a)(2) was revised to read in part, "A legible copy of: (i) Each foreign patent; (ii) Each publication or that portion which caused it to be listed, other than U.S. patents and U.S. patent application publications unless required by the

Office." Therefore applicant(s) has (have) not submitted copies of the cited U.S. patents and/or published patent applications with this Information Disclosure Statement.

In accordance with 37 C.F.R. §1.97(g) and (h), the filing of this Information Disclosure Statement should not be construed to mean that a search has been made or that no other material information as defined in 37 C.F.R. §1.56(b) exists.

☒ BEFORE FIRST OFFICE ACTION: Under §1.97(b)(3), this Information Disclosure Statement is being filed before the mailing date of a first Office Action on the merits. Although it is believed no fee is necessary, the Commissioner is authorized to charge any required fees to our Deposit Account No. 06-0308.
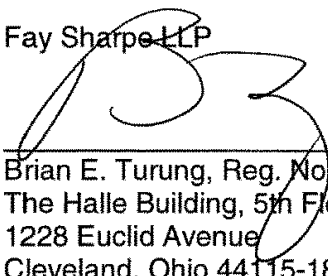
It is respectfully requested that the documents listed on Form PTO/SB/08a be considered and officially cited in examination of this application.

Respectfully submitted,
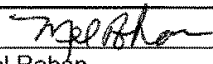
Fay Sharpe LLP

September 20, 2017
Date

Brian E. Turung, Reg. No. 35394
The Halle Building, 5th Floor
1228 Euclid Avenue
Cleveland, Ohio 44115-1843
216.363.9000

Certificate of Transmission or Mailing
I hereby certify that this correspondence (and any item referred to herein as being attached or enclosed) is (are) being ☒ transmitted to the USPTO by electronic transmission via EFS-Web on the date indicated below.
September 20, 2017   Mel Rohan Date

POWD 200033US02 4082350 1

2

UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICATION NUMBER	FILING or 371(c) DATE	GRP ART UNIT	FIL FEE REC'D	ATTY.DOCKET.NO	TOT CLAIMS	IND CLAIMS
15/641,439	07/05/2017	1735	850	POWD 200033US01	23	2

CONFIRMATION NO. 2533

27885
FAY SHARPE LLP
1228 Euclid Avenue, 5th Floor
The Halle Building
Cleveland, OH 44115

FILING RECEIPT

OC000000092713707

Date Mailed: 07/12/2017

Receipt is acknowledged of this non-provisional patent application. The application will be taken up for examination in due course. Applicant will be notified as to the results of the examination. Any correspondence concerning the application must include the following identification information: the U.S. APPLICATION NUMBER, FILING DATE, NAME OF APPLICANT, and TITLE OF INVENTION. Fees transmitted by check or draft are subject to collection. Please verify the accuracy of the data presented on this receipt. **If an error is noted on this Filing Receipt, please submit a written request for a Filing Receipt Correction. Please provide a copy of this Filing Receipt with the changes noted thereon. If you received a "Notice to File Missing Parts" for this application, please submit any corrections to this Filing Receipt with your reply to the Notice. When the USPTO processes the reply to the Notice, the USPTO will generate another Filing Receipt incorporating the requested corrections**

Inventor(s)
> Brian P. Doud, Cleveland Heights, OH;
> Nicholas J. Farkas, Euclid, OH;
> Andrew J. Sherman, Mentor, OH;

Applicant(s)
> Terves Inc., Euclid, OH;

Assignment For Published Patent Application
> Terves Inc.

Power of Attorney: None

Domestic Priority data as claimed by applicant
> This application is a DIV of 14/689,295 04/17/2015
> which claims benefit of 61/981,425 04/18/2014

Foreign Applications for which priority is claimed (You may be eligible to benefit from the **Patent Prosecution Highway** program at the USPTO. Please see http://www.uspto.gov for more information.) - None.
Foreign application information must be provided in an Application Data Sheet in order to constitute a claim to foreign priority. See 37 CFR 1.55 and 1.76.

Permission to Access Application via Priority Document Exchange: Yes

Permission to Access Search Results: No

Applicant may provide or rescind an authorization for access using Form PTO/SB/39 or Form PTO/SB/69 as appropriate.

ECOMETAL-002334

If Required, Foreign Filing License Granted: 07/12/2017

The country code and number of your priority application, to be used for filing abroad under the Paris Convention, is **US 15/641,439**

Projected Publication Date: 10/19/2017

Non-Publication Request: No

Early Publication Request: No
** SMALL ENTITY **
Title

        Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools

Preliminary Class

      164

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications: No

PROTECTING YOUR INVENTION OUTSIDE THE UNITED STATES

Since the rights granted by a U.S. patent extend only throughout the territory of the United States and have no effect in a foreign country, an inventor who wishes patent protection in another country must apply for a patent in a specific country or in regional patent offices. Applicants may wish to consider the filing of an international application under the Patent Cooperation Treaty (PCT). An international (PCT) application generally has the same effect as a regular national patent application in each PCT-member country. The PCT process **simplifies** the filing of patent applications on the same invention in member countries, but **does not result** in a grant of "an international patent" and does not eliminate the need of applicants to file additional documents and fees in countries where patent protection is desired.

Almost every country has its own patent law, and a person desiring a patent in a particular country must make an application for patent in that country in accordance with its particular laws. Since the laws of many countries differ in various respects from the patent law of the United States, applicants are advised to seek guidance from specific foreign countries to ensure that patent rights are not lost prematurely.

Applicants also are advised that in the case of inventions made in the United States, the Director of the USPTO must issue a license before applicants can apply for a patent in a foreign country. The filing of a U.S. patent application serves as a request for a foreign filing license. The application's filing receipt contains further information and guidance as to the status of applicant's license for foreign filing.

Applicants may wish to consult the USPTO booklet, "General Information Concerning Patents" (specifically, the section entitled "Treaties and Foreign Patents") for more information on timeframes and deadlines for filing foreign patent applications. The guide is available either by contacting the USPTO Contact Center at 800-786-9199, or it can be viewed on the USPTO website at http://www.uspto.gov/web/offices/pac/doc/general/index.html.

For information on preventing theft of your intellectual property (patents, trademarks and copyrights), you may wish to consult the U.S. Government website, http://www.stopfakes.gov. Part of a Department of Commerce initiative, this website includes self-help "toolkits" giving innovators guidance on how to protect intellectual property in specific countries such as China, Korea and Mexico. For questions regarding patent enforcement issues, applicants may call the U.S. Government hotline at 1-866-999-HALT (1-866-999-4258).

LICENSE FOR FOREIGN FILING UNDER

Title 35, United States Code, Section 184

Title 37, Code of Federal Regulations, 5.11 & 5.15

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The applicant has been granted a license under 35 U.S.C. 184, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" followed by a date appears on this form. Such licenses are issued in all applications where the conditions for issuance of a license have been met, regardless of whether or not a license may be required as set forth in 37 CFR 5.15. The scope and limitations of this license are set forth in 37 CFR 5.15(a) unless an earlier license has been issued under 37 CFR 5.15(b). The license is subject to revocation upon written notification. The date indicated is the effective date of the license, unless an earlier license of similar scope has been granted under 37 CFR 5.13 or 5.14.

This license is to be retained by the licensee and may be used at any time on or after the effective date thereof unless it is revoked. This license is automatically transferred to any related applications(s) filed under 37 CFR 1.53(d). This license is not retroactive.

The grant of a license does not in any way lessen the responsibility of a licensee for the security of the subject matter as imposed by any Government contract or the provisions of existing laws relating to espionage and the national security or the export of technical data. Licensees should apprise themselves of current regulations especially with respect to certain countries, of other agencies, particularly the Office of Defense Trade Controls, Department of State (with respect to Arms, Munitions and Implements of War (22 CFR 121-128)); the Bureau of Industry and Security, Department of Commerce (15 CFR parts 730-774); the Office of Foreign AssetsControl, Department of Treasury (31 CFR Parts 500+) and the Department of Energy.

NOT GRANTED

No license under 35 U.S.C. 184 has been granted at this time, if the phrase "IF REQUIRED, FOREIGN FILING LICENSE GRANTED" DOES NOT appear on this form. Applicant may still petition for a license under 37 CFR 5.12, if a license is desired before the expiration of 6 months from the filing date of the application. If 6 months has lapsed from the filing date of this application and the licensee has not received any indication of a secrecy order under 35 U.S.C. 181, the licensee may foreign file the application pursuant to 37 CFR 5.15(b).

SelectUSA

The United States represents the largest, most dynamic marketplace in the world and is an unparalleled location for business investment, innovation, and commercialization of new technologies. The U.S. offers tremendous resources and advantages for those who invest and manufacture goods here. Through SelectUSA, our nation works to promote and facilitate business investment. SelectUSA provides information assistance to the international investor community; serves as an ombudsman for existing and potential investors; advocates on behalf of U.S. cities, states, and regions competing for global investment; and counsels U.S. economic development organizations on investment attraction best practices. To learn more about why the United States is the best country in the world to develop technology, manufacture products, deliver services, and grow your business, visit http://www.SelectUSA.gov or call +1-202-482-6800.

PATENT APPLICATION FEE DETERMINATION RECORD Substitute for Form PTO-875		Application or Docket Number 15/641,439

APPLICATION AS FILED - PART I

	(Column 1)	(Column 2)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
FOR	NUMBER FILED	NUMBER EXTRA	RATE($)	FEE($)		RATE($)	FEE($)
BASIC FEE (37 CFR 1.16(a), (b), or (c))	N/A	N/A	N/A	70		N/A	
SEARCH FEE (37 CFR 1.16(k), (i), or (m))	N/A	N/A	N/A	300		N/A	
EXAMINATION FEE (37 CFR 1.16(o), (p), or (q))	N/A	N/A	N/A	360		N/A	
TOTAL CLAIMS (37 CFR 1.16(i))	23 minus 20 =	* 3	x 40 =	120	OR		
INDEPENDENT CLAIMS (37 CFR 1.16(h))	2 minus 3 =	*	x 210 =	0.00			
APPLICATION SIZE FEE (37 CFR 1.16(s))	If the specification and drawings exceed 100 sheets of paper, the application size fee due is $310 ($155 for small entity) for each additional 50 sheets or fraction thereof. See 35 U.S.C. 41(a)(1)(G) and 37 CFR 1.16(s).			0.00			
MULTIPLE DEPENDENT CLAIM PRESENT (37 CFR 1.16(j))				0.00			
* If the difference in column 1 is less than zero, enter "0" in column 2.			TOTAL	850		TOTAL	

APPLICATION AS AMENDED - PART II

		(Column 1)		(Column 2)	(Column 3)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
AMENDMENT A	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

		(Column 1)		(Column 2)	(Column 3)	SMALL ENTITY		OR	OTHER THAN SMALL ENTITY	
		CLAIMS REMAINING AFTER AMENDMENT		HIGHEST NUMBER PREVIOUSLY PAID FOR	PRESENT EXTRA	RATE($)	ADDITIONAL FEE($)		RATE($)	ADDITIONAL FEE($)
AMENDMENT B	Total (37 CFR 1.16(i))	*	Minus	**	=	x =		OR	x =	
	Independent (37 CFR 1.16(h))	*	Minus	***	=	x =		OR	x =	
	Application Size Fee (37 CFR 1.16(s))									
	FIRST PRESENTATION OF MULTIPLE DEPENDENT CLAIM (37 CFR 1.16(j))							OR		
						TOTAL ADD'L FEE		OR	TOTAL ADD'L FEE	

* If the entry in column 1 is less than the entry in column 2, write "0" in column 3.
** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 20, enter "20".
*** If the "Highest Number Previously Paid For" IN THIS SPACE is less than 3, enter "3".
The "Highest Number Previously Paid For" (Total or Independent) is the highest found in the appropriate box in column 1.

ECOMETAL-002337

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

SMALL ENTITY NEW APPLICATION TRANSMITTAL LETTER

Transmitted herewith for filing is the patent application entitled

Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools

Inventor(s): Brian P. Doud, Nicholas J. Farkas, Andrew J. Sherman

1. **Type of Application**

    ☒ Original (non-provisional)

2. **Required Papers Enclosed under 37 CFR 1.53(b) (Regular):**

    <u>24</u> Pages of specification

    <u>5</u> Pages of claims

    <u>1</u> Page of Abstract

    <u>4</u> Sheets of Drawings (Figures 1-4)

3. **Declaration or oath**

    ☒ Enclosed

4. **Preliminary Amendment**

    ☒ Enclosed

5. **Application Data Sheet (PTO/SB/14)**

    ☒ Enclosed

6. **Assignment**

    An assignment of the above-identified application to **TERVES INC.** is being filed via the Electronic Patent Assignment System (EPAS).

7. **Information Disclosure Statement**

    ☐ Enclosed   ☐ Substitute 1449 Form   ☐ PTO/SB/08 Form   References

8. ☐ **Nonpublication Request Under 35 USC 122(b)(2)(B)(i)** (Applicant(s) must attach form PTO/5B/35 or its equivalent.)

9. ☒ **Applicant(s) claim(s) small entity status under 37 CFR 1.27.**

10. Fee Calculation (37 CFR 1.16)

CLAIMS AS FILED, LESS ANY CLAIMS CANCELED BY ABOVE-INDICATED AMENDMENT(S)				
(1) FOR	(2) NUMBER FILED	(3) NUMBER EXTRA	(4) RATE	(5) CALCULATIONS
TOTAL CLAIMS (37 CFR 1.16(c))	23 - 20 =	3	x $40.00	= $120.00
INDEPENDENT CLAIMS (37 CFR 1.16(B))	2 - 3 =	0	x $210.00	= $0.00
MULTIPLE DEPENDENT CLAIMS (IF APPLICABLE) (37 CFR 1.16(D))		ANY - - 0	x $390.00	= $0.00
UTILITY APPLICATION SIZE FEE (FOR APPLICATION THAT EXCEEDS 100 SHEETS, FEE FOR EACH GROUP OF 50 ADDITIONAL SHEETS)	0 GROUP(S)		x $200.00	= $0.00
BASIC FEE (37 CFR 1.16(a))				$70.00
UTILITY SEARCH FEE				$300.00
UTILITY EXAMINATION FEE				$360.00
TOTAL SMALL ENTITY FEE =				**$850.00**

11. Method of Payment

☒ The fees indicated above are authorized to be charged to a credit card. The fee(s) is/are being submitted via EFS-Web. If the credit card is unable to be charged, please charge any and all fees or credit any overpayment to Deposit Account No. 06-0308. If there are any additional fees required by this communication, please charge same to Deposit Account No. 06-0308.

This is an authorization under 37 CFR 1.136(a)(3) to treat any concurrent or future reply, requiring a petition for extension of time, as incorporating a petition for the appropriate extension of time.

12. Examination Fee

☐ Applicant(s) has/have not paid the examination fee at this time.

13. Please address correspondence to:

CUSTOMER NUMBER 27885

2

14.   **Please direct telephone calls to:**

Brian E. Turung, Telephone: 216.363.9000

Facsimile: 216.363.9001

Email: uspto@faysharpe.com

Respectfully submitted,

Fay Sharpe LLP

July 5, 2017
Date

Brian E. Turung, Reg. No. 35394
The Halle Building, 5th Floor
1228 Euclid Avenue
Cleveland, Ohio 44115-1843
216.363.9000

Certificate of Transmission or Mailing
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July 5, 2017	
Date	Mel Rohan

POWD 200033US02 4054917 1

3

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	POWD 200033US01
	Application Number	

Title of Invention	Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools

The application data sheet is part of the provisional or nonprovisional application for which it is being submitted. The following form contains the bibliographic data arranged in a format specified by the United States Patent and Trademark Office as outlined in 37 CFR 1.76.
This document may be completed electronically and submitted to the Office in electronic format using the Electronic Filing System (EFS) or the document may be printed and included in a paper filed application.

Secrecy Order 37 CFR 5.2

☐ Portions or all of the application associated with this Application Data Sheet may fall under a Secrecy Order pursuant to 37 CFR 5.2 (Paper filers only. Applications that fall under Secrecy Order may not be filed electronically.)

Inventor Information:

Inventor 1   [Remove]
Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Brian	P.	Doud	

Residence Information (Select One) ● US Residency   Non US Residency   Active US Military Service

City	Cleveland Heights	State/Province	OH	Country of Residence	US

Mailing Address of Inventor:

Address 1	3414 Meadow Brook Blvd.
Address 2	
City	Cleveland Heights	State/Province	OH
Postal Code	44118	Country i	US

Inventor 2   [Remove]
Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Nicholas	J.	Farkas	

Residence Information (Select One) ⦿ US Residency   Non US Residency   Active US Military Service

City	Euclid	State/Province	OH	Country of Residence	US

Mailing Address of Inventor:

Address 1	24112 Rock Well Drive
Address 2	
City	Euclid	State/Province	OH
Postal Code	44118	Country i	US

Inventor 3   [Remove]
Legal Name

Prefix	Given Name	Middle Name	Family Name	Suffix
	Andrew	J.	Sherman	

Residence Information (Select One) ⦿ US Residency   Non US Residency   Active US Military Service

PTO/AIA/14 (12-13)
Approved for use through 01/31/2014. OMB 0651-0032
U.S. Patent and Trademark Office; U.S. DEPARTMENT OF COMMERCE
Under the Paperwork Reduction Act of 1995, no persons are required to respond to a collection of information unless it contains a valid OMB control number.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	POWD 200033US01
	Application Number	

Title of Invention	Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools

City	Mentor	State/Province	OH	Country of Residence	US

Mailing Address of Inventor:

Address 1	9181 Boyer Lane		
Address 2			
City	Mentor	State/Province	OH
Postal Code	44060	Country i	US

All Inventors Must Be Listed - Additional Inventor Information blocks may be generated within this form by selecting the **Add** button.

[Add]

Correspondence Information:

Enter either Customer Number or complete the Correspondence Information section below.
For further information see 37 CFR 1.33(a).

☐ An Address is being provided for the correspondence Information of this application.

Customer Number	27885
Email Address		[Add Email] [Remove Email]

Application Information:

Title of the Invention	Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools	
Attorney Docket Number	POWD 200033US01	**Small Entity Status Claimed** ☒
Application Type	Nonprovisional	
Subject Matter	Utility	
Total Number of Drawing Sheets (if any)	4	**Suggested Figure for Publication (if any)** 4

Filing By Reference :

Only compete this section when filing an application by reference under 35 U.S.C. 111(c) and 37 CFR 1.57(a). Do not complete this section if application papers including a specification and any drawings are being filed. Any domestic benefit or foreign priority information must be provided in the appropriate section(s) below (i.e., "Domestic Benefit/National Stage Information" and "Foreign Priority Information").

For the purposes of a filing date under 37 CFR 1.53(b), the description and any drawings of the present application are replaced by this reference to the previously filed application, subject to conditions and requirements of 37 CFR 1.57(a).

Application number of the previously filed application	Filing date (YYYY-MM-DD)	Intellectual Property Authority or Country

Publication Information:

☐ Request Early Publication (Fee required at time of Request 37 CFR 1.219)

☐ **Request Not to Publish.** I hereby request that the attached application not be published under 35 U.S.C. 122(b) and certify that the invention disclosed in the attached application **has not and will not** be the subject of an application filed in another country, or under a multilateral international agreement, that requires publication at eighteen months after filing.

Application Data Sheet 37 CFR 1.76	Attorney Docket Number	POWD 200033US01
	Application Number	

Title of Invention	Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools

Representative Information:

Representative information should be provided for all practitioners having a power of attorney in the application. Providing this information in the Application Data Sheet does not constitute a power of attorney in the application (see 37 CFR 1.32).
Either enter Customer Number or complete the Representative Name section below. If both sections are completed the customer Number will be used for the Representative Information during processing.

Please Select One:	● Customer Number	US Patent Practitioner	○ Limited Recognition (37 CFR 11.9)
Customer Number	27885		

Domestic Benefit/National Stage Information:

This section allows for the applicant to either claim benefit under 35 U.S.C. 119(e), 120, 121, or 365(c) or indicate National Stage entry from a PCT application. Providing this information in the application data sheet constitutes the specific reference required by 35 U.S.C. 119(e) or 120, and 37 CFR 1.78.
When referring to the current application, please leave the application number blank.

Prior Application Status	Pending	▼		Remove
Application Number	Continuity Type		Prior Application Number	Filing Date (YYYY-MM-DD)
	Division of	▼	14689295	2015-04-17
Prior Application Status	Expired	▼		Remove
Application Number	Continuity Type		Prior Application Number	Filing Date (YYYY-MM-DD)
14689295	Claims benefit of provisional	▼	61981425	2014-04-18

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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	POWD 200033US01
	Application Number	

Title of Invention	Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools

Statement under 37 CFR 1.55 or 1.78 for AIA (First Inventor to File) Transition Applications

| ☐ | This application (1) claims priority to or the benefit of an application filed before March 16, 2013 and (2) also contains, or contained at any time, a claim to a claimed invention that has an effective filing date on or after March 16, 2013.
NOTE: By providing this statement under 37 CFR 1.55 or 1.78, this application, with a filing date on or after March 16, 2013, will be examined under the first inventor to file provisions of the AIA. |
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Application Data Sheet 37 CFR 1.76	Attorney Docket Number	POWD 200033US01
	Application Number	

Title of Invention	Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools

Applicant 1 [Remove]

If the applicant is the inventor (or the remaining joint inventor or inventors under 37 CFR 1.45), this section should not be completed. The information to be provided in this section is the name and address of the legal representative who is the applicant under 37 CFR 1.43; or the name and address of the assignee, person to whom the inventor is under an obligation to assign the invention, or person who otherwise shows sufficient proprietary interest in the matter who is the applicant under 37 CFR 1.46. If the applicant is an applicant under 37 CFR 1.46 (assignee, person to whom the inventor is obligated to assign, or person who otherwise shows sufficient proprietary interest) together with one or more joint inventors, then the joint inventor or inventors who are also the applicant should be identified in this section.

[Clear]

● Assignee	Legal Representative under 35 U.S.C. 117	Joint Inventor
Person to whom the inventor is obligated to assign.	Person who shows sufficient proprietary interest	

If applicant is the legal representative, indicate the authority to file the patent application, the inventor is:

[▼]

Name of the Deceased or Legally Incapacitated Inventor :	

If the Applicant is an Organization check here. ☒

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| **Application Data Sheet 37 CFR 1.76** | Attorney Docket Number | POWD 200033US01 |
| | Application Number | |

| Title of Invention | Galvanically-Active In Situ Formed Particles for Controlled Rate Dissolving Tools |

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Signature	/bet/			Date (YYYY-MM-DD)	2017-07-05
First Name	Brian E.	Last Name	Turung	Registration Number	35394

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GALVANICALLY-ACTIVE *INSITU* FORMED PARTICLES
FOR CONTROLLED RATE DISSOLVING TOOLS

[0001]   The present invention is a divisional of United States Patent Application Serial No. 14/689,295 filed April 17, 2015, which in turn claims priority on United States Provisional Patent Application Serial No. 61/981,425 filed April 18, 2014, which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002]   The present invention is directed to a novel magnesium composite for use as a dissolvable component in oil drilling.

BACKGROUND OF THE INVENTION

[0003]   The ability to control the dissolution of a down hole well component in a variety of solutions is very important to the utilization of non-drillable completion tools, such as sleeves, frac balls, hydraulic actuating tooling, and the like.   Reactive materials for this application, which dissolve or corrode when exposed to acid, salt, and/or other wellbore conditions, have been proposed for some time.   Generally, these components consist of materials that are engineered to dissolve or corrode.   Dissolving polymers and some powder metallurgy metals have been disclosed, and are also used extensively in the pharmaceutical industry for controlled release of drugs.   Also, some medical devices have been formed of metals or polymers that dissolve in the body.

[0004]   While the prior art well drill components have enjoyed modest success in reducing well completion costs, their consistency and ability to specifically control dissolution rates in specific solutions, as well as other drawbacks such as limited strength and poor reliability, have impacted their ubiquitous adoption.   Ideally, these components would be manufactured by a process that is low cost, scalable, and produces a controlled corrosion rate having similar or increased strength as compared to traditional engineering alloys such as aluminum, magnesium, and iron.   Ideally, traditional heat treatments, deformation processing, and machining techniques could be used on the components without impacting the dissolution rate and reliability of such components.

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SUMMARY OF THE INVENTION

[0005]   The present invention is directed to a novel magnesium composite for use as a dissolvable component in oil drilling and will be described with particular reference to such application.   As can be appreciated, the novel magnesium composite of the present invention can be used in other applications (e.g., non-oil wells, etc.).   In one non-limiting embodiment, the present invention is directed to a ball or other tool component in a well drilling or completion operation such as, but not limited to, a component that is seated in a hydraulic operation that can be dissolved away after use so that no drilling or removal of the component is necessary.   Tubes, valves, valve components, plugs, frac balls, and other shapes and components can "also be formed of the novel magnesium composite of the present invention.   For purposes of this invention, primary dissolution is measured for valve components and plugs as the time the part removes itself from the seat of a valve or plug arrangement or can become free floating in the system.   For example, when the part is a plug in a plug system, primary dissolution occurs when the plug has degraded or dissolved to a point that it can no long function as a plug and thereby allows fluid to flow about the plug.   For purposes of this invention, secondary dissolution is measured in the time the part is fully dissolved into sub-mm particles.   As can be appreciated, the novel magnesium composite of the present invention can be used in other well components that also desire the function of dissolving after a period of time.   In one non-limiting aspect of the present invention, a galvanically-active phase is precipitated from the novel magnesium composite composition and is used to control the dissolution rate of the component; however, this is not required.   The novel magnesium composite is generally castable and/or machinable, and can be used in place of existing metallic or plastic components in oil and gas drilling rigs including, but not limited to, water injection and hydraulic fracturing.   The novel magnesium composite can be heat treated as well as extruded and/or forged.

[0006]   In one non-limiting aspect of the present invention, the novel magnesium composite is used to form a castable, moldable, or extrudable component.   Non-limiting magnesium composites in accordance with the present invention include at least 50 wt.% magnesium.   One or more additives are added to a magnesium or magnesium alloy to form the novel magnesium composite of the present invention.   The one or more additives can be selected and used in quantities so that galvanically-active intermetallic or insoluble precipitates form in the magnesium or magnesium alloy while the magnesium or magnesium alloy is in a molten state and/or during

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the cooling of the melt; however, this is not required. The one or more additives typically are added in a weight percent that is less than a weight percent of said magnesium or magnesium alloy. Typically, the magnesium or magnesium alloy constitutes about 50.1 wt%99.9 wt% of the magnesium composite and all values and ranges therebetween. In one non-limiting aspect of the invention, the magnesium or magnesium alloy constitutes about 60 wt.%-95 wt.% of the magnesium composite, and typically the magnesium or magnesium alloy constitutes about 70 wt.%-90 wt.% of the magnesium composite. The one or more additives are typically added to the molten magnesium or magnesium alloy at a temperature that is less than the melting point of the one or more additives. The one or more additives generally have an average particle diameter size of at least about 0.1 microns, typically no more than about 500 microns (e.g., 0.1 microns, 0.1001 microns, 0.1002 microns ... 499.9998 microns, 499.9999 microns, 500 microns) and including any value or range therebetween, more typically about 0.1 to 400 microns, and still more typically about 10 to 50 microns. During the process of mixing the one or more additives in the molten magnesium or magnesium alloy, the one or more additives are typically not caused to fully melt in the molten magnesium or magnesium alloy. As can be appreciated, the one or more additives can be added to the molten magnesium or magnesium alloy at a temperature that is greater than the melting point of the one or more additives. In such a method of forming the magnesium composite, the one or more additives form secondary metallic alloys with the magnesium and/or other metals in the magnesium alloy, said secondary metallic alloys having a melting point that is greater than the magnesium and/or other metals in the magnesium alloy. As the molten metal cools, these newly formed secondary metallic alloys begin to precipitate out of the molten metal and form the *in situ* phase to the matrix phase in the cooled and solid magnesium composite. After the mixing process is completed, the molten magnesium or magnesium alloy and the one or more additives that are mixed in the molten magnesium or magnesium alloy are cooled to form a solid component. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 10°C less than the melting point of the additive added to the molten magnesium or magnesium alloy during the addition and mixing process, typically at least about 100°C less than the melting point of the additive added to the molten magnesium or magnesium alloy during the addition and mixing process, more typically about 100°C-1000°C (and any value or range therebetween) less than the melting point of the additive added to the molten magnesium or magnesium alloy during the addition and mixing process; however, this is

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not required. The never melted particles and/or the newly formed secondary metallic alloys are referred to as *in situ* particle formation in the molten magnesium composite. Such a process can be used to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite.

[0007] The invention adopts a feature that is usually a negative in traditional casting practices wherein a particle is formed during the melt processing that corrodes the alloy when exposed to conductive fluids and is imbedded in eutectic phases, the grain boundaries, and/or even within grains with precipitation hardening. This feature results in the ability to control where the galvanically-active phases are located in the final casting, as well as the surface area ratio of the *in situ* phase to the matrix phase, which enables the use of lower cathode phase loadings as compared to a powder metallurgical or alloyed composite to achieve the same dissolution rates. The *in situ* formed galvanic additives can be used to enhance mechanical properties of the magnesium composite such as ductility, tensile strength, and/or shear strength. The final magnesium composite can also be enhanced by heat treatment as well as deformation processing (such as extrusion, forging, or rolling) to further improve the strength of the final composite over the as-cast material; however, this is not required. The deformation processing can be used to achieve strengthening of the magnesium composite by reducing the grain size of the magnesium composite. Further enhancements, such as traditional alloy heat treatments (such as solutionizing, aging and/or cold working) can be used to enable control of dissolution rates though precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties; however, this is not required. Because galvanic corrosion is driven by both the electro potential between the anode and cathode phase, as well as the exposed surface area of the two phases, the rate of corrosion can also be controlled through adjustment of the *in situ* formed particles size, while not increasing or decreasing the volume or weight fraction of the addition, and/or by changing the volume/weight fraction without changing the particle size. Achievement of *in situ* particle size control can be achieved by mechanical agitation of the melt, ultrasonic processing of the melt, controlling cooling rates, and/or by performing heat treatments. *In situ* particle size can also or alternatively be modified by secondary processing such as rolling, forging, extrusion and/or other deformation techniques.

[0008] In another non-limiting aspect of the invention, a cast structure can be made into alinost any shape. During formation, the active galvanically-active *in situ* phases can be

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uniformly dispersed throughout the component and the grain or the grain boundary composition can be modified to achieve the desired dissolution rate. The galvanic corrosion can be engineered to affect only the grain boundaries and/or can affect the grains as well (based on composition); however, this is not required. This feature can be used to enable fast dissolutions of high-strength lightweight alloy composites with significantly less active (cathode) *in situ* phases as compared to other processes.

[0009] In still another and/or alternative non-limiting aspect of the invention, ultrasonic processing can be used to control the size of the *in situ* formed galvanically-active phases; however, this is not required.

[0010] In yet another and/or alternative non-limiting aspect of the invention, the *in situ* formed particles can act as matrix strengtheners to further increase the tensile strength of the material compared to the base alloy without the additive; however, this is not required.

[0011] In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method of controlling the dissolution properties of a metal selected from the class of magnesium and/or magnesium alloy comprising of the steps of a) melting the magnesium or magnesium alloy to a point above its solidus, b) introducing an additive material and/or phase to the magnesium or magnesium alloy in order to achieve *in situ* precipitation of galvanically-active intermetallic phases, and c) cooling the melt to a solid form. The additive material is generally added to the magnesium or magnesium alloy when the magnesium or magnesium alloy is in a molten state and at a temperature that is less than the melting point of the additive material. The galvanically-active intermetallic phases can be used to enhance the yield strength of the alloy; however, this is not required. The size of the *in situ* precipitated intermetallic phase can be controlled by a melt mixing technique and/or cooling rate; however, this is not required. The method can include the additional step of subjecting the magnesium composite to intermetallic precipitates to solutionizing of at least about 300°C to improve tensile strength and/or improve ductility; however, this is not required. The solutionizing temperature is less than the melting point of the magnesium composite. Generally, the solutionizing temperature is less than 50°C-200°C (the melting point of the magnesium composite) and the time period of solutionizing is at least 0.1 hours. In one non-limiting aspect of the invention, the magnesium composite can be subjected to a solutionizing temperature for about 0.5-50 hours (e.g., 1-15 hours, etc.) at a temperature of 300°C-620°C (e.g., 300°C -500°C, etc.). The method can include the additional

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step of subjecting the magnesium composite to intermetallic precipitates and to artificially age the magnesium composite at a temperature at least about 90°C to improve the tensile strength; however, this is not required. The artificially aging process temperature is typically less than the solutionizing temperature and the time period of the artificially aging process temperature is typically at least 0.1 hours. Generally, the artificially aging process is less than 50°C-400°C (the solutionizing temperature). In one non-limiting aspect of the invention, the magnesium composite can be subjected to aging treatment for about 0.5-50 hours (e.g., 1-16 hours, etc.) at a temperature of 90°C -300°C (e.g., 100°C-200°C).

[0012] In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and about 0.05-35 wt.% nickel (and all values or ranges therebetween) is added to the magnesium or magnesium alloy to form intermetallic Mg_2Ni as a galvanically-active *in situ* precipitate. In one non-limiting arrangement, the magnesium composite includes about 0.05-23.5 wt.% nickel, 0.01-5 wt.% nickel, 3-7 wt.% nickel, 7-10 wt.% nickel, or 10-24.5 wt.% nickel. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni, and any unalloyed nickel particles· are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

[0013] In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and about 0.05-35 wt.% copper (and all values or ranges therebetween) is added to the magnesium or magnesium alloy to form intermetallic $CuMg_2$ as the galvanically-active *in situ* precipitate. In one non-limiting arrangement, the magnesium composite includes about 0.01-5 wt.% copper, about 0.5-15 wt.% copper, about 15-35 wt.% copper, or about 0.01-20 wt.%. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less

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than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of $CuMg_2$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $CuMg_2$, and any unalloyed copper particles are cooled and an *in situ* precipitate of solid particles of $CuMg_2$ and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy.

[0014] In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and about 0.05-20% by weight cobalt is added to the magnesium or magnesium alloy to form an intermetallic $CoMg_2$ as the galvanically-active *in situ* precipitate. The cobalt is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. During the mixing process, solid particles of $CoMg_2$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $COMg_2$, and any unalloyed cobalt particles are cooled and an *in situ* precipitate of solid particles of $CoMg_2$ and any unalloyed cobalt particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the cobalt added to the molten magnesium or magnesium alloy.

[0015] In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and cobalt is added to the magnesium or magnesium alloy which forms an intermetallic Mg_xCo as the galvanically-active particle *in situ* precipitate. The cobalt is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the cobalt. During the mixing process, solid particles of $CoMg_x$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $CoMg_x$, and any unalloyed cobalt particles are cooled and an *in situ* precipitate of solid particles of $CoMg_x$ and any unalloyed cobalt particles are formed in the solid

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magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the cobalt added to the molten magnesium or magnesium alloy.

[0016] In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and about 0.5-35% by weight of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is faster than 1°C per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of $SMMg_x$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $SMMg_x$, and any unalloyed secondary metal particles are cooled and an *in situ* precipitate of solid particles of $SMMg_x$ and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

[0017] In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and about 0.5-35% by weight of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanicallyactive intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is slower than 1°C per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of SMM& are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $SMMg_x$, and any unalloyed secondary metal particles are cooled and an *in situ* precipitate of solid particles of $SMMg_x$ and any unalloyed secondary metal

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particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

[0018] In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and about 0.05-35 wt.% of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is faster than 0.01°C per min and slower than 1°C per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of $SMMg_x$ are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of $SMMg_x$ and any unalloyed secondary metal particles are cooled and an *in situ* precipitate of solid particles of $SMMg_x$, and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

[0019] In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and about 0.05-35 wt.% of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is faster than 10°C per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of $SMMg_x$ were formed. Once the mixing process was completed, the mixture of molten

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magnesium or magnesium alloy, solid particles of $SMMg_x$, and any unalloyed secondary metal particles are cooled and an *in situ* precipitate of solid particles of $SMMg_x$ and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

[0020]   In still yet another andlor alternative non-limiting aspect of the invention, there is provided magnesium composite that is over 50 wt.% magnesium and about 0.5-35 wt.% of secondary metal (SM) is added to the magnesium or magnesium alloy to form a galvanically--active intermetallic particle when compared to magnesium or a magnesium alloy in the remaining casting where the cooling rate between the liquidus to the solidus is slower than 10°C per minute. The secondary metal is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the secondary metal. During the mixing process, solid particles of SMMgx are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of SMMgx, and any unalloyed secondary metal particles are cooled and an in situ precipitate of solid particles of SMMgx and any unalloyed secondary metal particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the secondary metal added to the molten magnesium or magnesium alloy. As can be appreciated, one or more secondary metals can be added to the molten magnesium or magnesium alloy.

[0021]   In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium alloy that includes over 50 wt.% magnesium and includes at least one metal selected from the group consisting of aluminum in an amount of about 0.5-10 wt.%, zinc in amount of about 0.05-6 wt.%, zirconium in an amount of about 0.01-3 wt.%, and/or manganese in an amount of about 0.15-2 wt.%. In one non-limiting formulation, the magnesium alloy that includes over 50 wt.% magnesium and includes at least one metal selected from the group consisting of zinc in amount of about 0.05-6 wt.%, zirconium in an amount of about 0.05-3 wt.%, manganese in an amount of about 0.05-0.25 wt.%, boron in an amount of about 0.0002-0.04 wt.%, and bismuth in

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an amount of about 0.4-0.7 wt.%. The magnesium alloy can then be heated to a molten state and one or more secondary metal (SM) (e.g., copper, nickel, cobalt, titanium, silicon, iron, etc.) can be added to the molten magnesium alloy which forms an intermetallic galvanically-active particle *in situ* precipitate. The galvanically-active particle can be $SMMg_x$, $SMAl_x$, $SMZn_x$, $SMZr_x$, $SMMn_x$, SMB_x, $SMBi_x$, SM in combination with anyone of B, Bi, Mg, Al, Zn, Zr, and Mn.

[0022]   In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and at least one metal selected from the group consisting of zinc in an amount of about 0.05-6 wt.%, zirconium in amount of about 0.05-3 wt.%, manganese in an amount of about 0.05-0.25 wt.%, boron in an amount of about 0.0002-0.04 wt.%, and/or bismuth in an amount of about 0.4-0.7 wt.% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The magnesium alloy can then be heated to a molten state and one or more secondary metal (SM) (e.g., copper, nickel, cobalt, titanium, iron, etc.) can be added to the molten magnesium alloy which forms an intermetallic galvanically-active particle *in situ* precipitate. The galvanically-active particle can be $SMMg_x$, $SMZn_x$, $SMZr_x$, $SMMn_x$, SMB_x, $SMBi_x$, SM in combination with anyone of Mg, Zn, Zr, Mn, B and/or Bi.

[0023]   In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium or magnesium alloy that is over 50 wt.% magnesium and nickel in an amount of about 0.01-5 wt.% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

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[0024] In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and nickel in an amount of from about 0.3-7 wt.% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

[0025] In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and nickel in an amount of about 7-10 wt.% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process was completed, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

[0026] In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and nickel in an amount of about 10-24.5 wt.% is added to the magnesium or magnesium alloy to form a galvanically-active

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intermetallic particle in the magnesium or magnesium alloy. The nickel is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the nickel. During the mixing process, solid particles of Mg_2Ni are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Ni, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Ni and any unalloyed nickel particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the nickel added to the molten magnesium or magnesium alloy during the addition and mixing process.

[0027]   In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and copper in an amount of about 0.01-5 wt.% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature 50 of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg_2Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Cu, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

[0028]   In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and includes copper in an amount of about 0.5-15 wt.% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the

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temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg_2Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Cu, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

[0029] In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and includes copper in an amount of about 15-35 wt.% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg_2Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of Mg_2Cu, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

[0030] In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is over 50 wt.% magnesium and includes copper in an amount of about 0.01-20 wt.% is added to the magnesium or magnesium alloy to form a galvanically-active intermetallic particle in the magnesium or magnesium alloy. The copper is added to the magnesium or magnesium alloy while the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. Throughout the mixing process, the temperature of the molten magnesium or magnesium alloy is less than the melting point of the copper. During the mixing process, solid particles of Mg_2Cu are formed. Once the mixing process is complete, the mixture of molten magnesium or magnesium alloy, solid particles of

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Mg_2Cu, and any unalloyed nickel particles are cooled and an *in situ* precipitate of solid particles of Mg_2Cu and any unalloyed copper particles are formed in the solid magnesium or magnesium alloy. Generally, the temperature of the molten magnesium or magnesium alloy is at least about 200°C less than the melting point of the copper added to the molten magnesium or magnesium alloy during the addition and mixing process.

[0031] In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to heat treatments such as solutionizing, aging and/or cold working to be used to control dissolution rates though precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties. The aging process (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours. The solutionizing (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours.

[0032] In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content is at least about 75% and nickel is added to form *in situ* precipitation of at least 0.05 wt.% $MgNi_2$ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500°C for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without nickel additions subjected to the said aging treatment.

[0033] In another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the magnesium content is at least about 85% and nickel is added to form *in situ* precipitation of at least 0.05 wt.% $MgNi_2$ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature at about 100-500°C for a period of 0.25-50 hours, the magnesium composite being characterized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of nickel.

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[0034] In still another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content in the alloy is at least about 75% and copper is added to form in situ precipitation of at least about 0.05 wt.% $MgCu_2$ with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500°C for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without copper additions subjected to the said aging treatment.

[0035] In yet another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the total content of magnesium in the magnesium or magnesium alloy is at least about 85 wt.% and copper is added to form in situ precipitation of at least 0.05 wt.% $MgCu_2$ with the magnesium or magnesium composite and solutionizing the resultant metal at a temperature of about 100-500°C for a period of 0.25-50 hours, the magnesium composite is characterized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of copper.

[0036] In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable ball or frac ball in hydraulic fracturing and well drilling.

[0037] In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable tool for use in well drilling and hydraulic control as well as hydraulic fracturing.

[0038] In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that includes secondary institute formed reinforcements that are not galvanically-active to the magnesium or magnesium alloy matrix to increase the mechanical properties of the magnesium composite. The secondary institute formed reinforcements include a Mg_2Si phase as the in situ formed reinforcement.

[0039] In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a faster cooling rate from the liquidus to the solidus point to create smaller in situ formed particles.

[0040] In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a slower cooling rate from the liquidus to the solidus point to create larger in situ formed particles.

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[0041]   In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to heat treatments such as solutionizing, aging and/or cold working to be used to control dissolution rates though precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties. The aging process (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours. The solutionizing (when used) can be for at least about 1 hour, for about 1-50 hours, for about 1-20 hours, or for about 8-20 hours.

[0042]   In still yet another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content is at least about 75% and nickel is added to form in situ precipitation of at least 0.05 wt.% MgNi2 with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500°C for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without nickel additions subjected to the said aging treatment.

[0043]   In another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the magnesium content is at least about 85% and nickel is added to form in situ precipitation of at least 0.05 wt.% MgNi2 with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature at about 100-500°C for a period of 0.25-50 hours, the magnesium composite being characterized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of nickel.

[0044]   In still another and/or alternative non-limiting aspect of the invention, there is provided a method for controlling the dissolution rate of the magnesium composite wherein the magnesium content in the alloy is at least about 75% and copper is added to form in situ precipitation of at least about 0.05 wt.% MgCu2 with the magnesium or magnesium alloy and solutionizing the resultant metal at a temperature within a range of 100-500°C for a period of 0.25-50 hours, the magnesium composite being characterized by higher dissolution rates than metal without copper additions subjected to the said aging treatment.

[0045]   In yet another and/or alternative non-limiting aspect of the invention, there is provided a method for improving the physical properties of the magnesium composite wherein the total content of magnesium in the magnesium or magnesium alloy is at least about 85 wt.% and copper is added to

form in situ precipitation of at least 0.05 wt.% MgCu2 with the magnesium or magnesium composite and solutionizing the resultant metal at a temperature of about 100-500°C for a period of 0.25-50 hours, the magnesium composite is characterized by higher tensile and yield strengths than magnesium base alloys of the same composition, but not including the amount of copper.

[0046]   In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable ball or frac ball in hydraulic fracturing and well drilling.

[0047]   In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite for use as a dissolvable tool for use in well drilling and hydraulic control as well as hydraulic fracturing.

[0048]   In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that includes secondary institute formed reinforcements that are not galvanically-active to the magnesium or magnesium alloy matrix to increase the mechanical properties of the magnesium composite. The secondary institute formed reinforcements include a Mg_2Si phase as the *in situ* formed reinforcement.

[0049]   In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a faster cooling rate from the liquidus to the solidus point to create smaller *in situ* formed particles.

[0050]   In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to a slower cooling rate from the liquidus to the solidus point to create larger *in situ* formed particles.

[0051]   In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to mechanical agitation during the cooling rate from the liquidus to the solidus point to create smaller *in situ* formed particles.

[0052]   In another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to mechanical agitation during the cooling rate from the liquidus to the solidus point to create smaller *in situ* formed particles.

[0053]   In still another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to chemical agitation during the cooling rate from the liquidus to the solidus point to create smaller *in situ* formed particles.

[0054] In yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to ultrasonic agitation during the cooling rate from the liquidus to the solidus point to create smaller *in situ* formed particles.

[0055] In still yet another and/or alternative non-limiting aspect of the invention, there is provided a magnesium composite that is subjected to deformation or extrusion to further improve dispersion of the *in situ* formed particles.

[0056] In another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having 9 wt.% aluminum, 1 wt.% zinc and 90 wt.% magnesium, b) melting the AZ91 D magnesium alloy to a temperature above 800°C, c) adding up to about 7 wt.% nickel to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of nickel, d) mixing the nickel with the melted AZ91D magnesium alloy and dispersing the nickel in the melted alloy using chemical mixing agents while maintaining the temperature below the melting point of nickel, and e) cooling and casting the melted mixture in a steel mold. The cast material has a tensile strength of about 14 ksi, and an elongation of about 3% and a shear strength of 11 ksi. The cast material has a dissolve rate of about 75 mg/cm^2-min in a 3% KCl solution at 90°C. The cast material dissolves at a rate of 1 mg/cm2-hr in a 3% KCl solution at 21°C. The cast material dissolves at a rate of 325mg/cm^2-hr. in a 3% KCl solution at 90°C. The cast material can be subjected to extrusion with a 11:1 reduction area. The extruded cast material exhibits a tensile strength of 40 ksi, and an elongation to failure of 12%. The extruded cast material dissolves at a rate of 0.8 mg/cm^2-min in a 3% KCl solution at 20°C. The extruded cast material dissolves at a rate of 100 mg/cm^2-hr. in a 3% KCl solution at 90°C. The extruded cast material can be subjected to an artificial T5 age treatment of 16 hours between 100°C-200°C. The aged extruded cast material exhibits a tensile strength of 48 ksi, an elongation to failure of 5%, and a shear strength of 25 ksi. The aged extruded cast material dissolves at a rate of 110 mg/cm^2-hr in 3% KCl solution at 90°C and 1 mg/cm^2-hr in 3% KCI solution at 20°C. The cast material can be subjected to a solutionizing treatment T4 for about 18 hours between 400°C-500°C and then subjected to an artificial T6 age treatment for about 16 hours between 100°C-200°C. The aged and solutionized cast material exhibits a tensile strength of about 34 ksi, an elongation to failure of about 11 %, and a shear strength of about 18 ksi. The aged and solutionized cast material

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dissolves at a rate of about 84mg/cm^2-hr in 3% KCl solution at 90°C, and about 0.8 mg/cm^2-hr in 3% KCl solution at 20°C.

[0057] In another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ91D magnesium alloy having 9 wt.% aluminum, 1 wt.% zinc and 90 wt.% magnesium, b) melting the AZ91D magnesium alloy to a temperature above 800°C, c) adding up to about 1 wt.% nickel to the melted AZ91D magnesium alloy at a temperature that is less than the melting point of nickel, d) mixing the nickel with the melted AZ91D magnesium alloy and dispersing the nickel in the melted alloy using chemical mixing agents while maintaining the temperature below the melting point of nickel, and e) cooling and casting the melted mixture in a steel mold. The cast material has a tensile strength of about 18 ksi, and an elongation of about 5% and a shear strength of 17ksi. The cast material has a dissolve rate of about 45 mg/cm2-min in a 3% KCl solution at 90°C. The cast material dissolves at a rate of 0.5 mg/cm^2-hr. in a 3% KCl solution at 21°C. The cast material dissolves at a rate of 325mg/cm^2-hr. in a 3% KCl solution at 90°C. The cast material was then subjected to extrusion with a 20:1 reduction area. The extruded cast material exhibits a tensile yeild strength of 35ksi, and an elongation to failure of 12%. The extruded cast material dissolves at a rate of 0.8 mg/cm^2-min in a 3% KCl solution at 20°C. The extruded cast material dissolves at a rate of 50mg/cm^2-hr in a 3% KCl solution at 90°C. The extruded cast material can be subjected to an artificial T5 age treatment of 16 hours between 100°C-200°C. The aged extruded cast material exhibits a tensile strength of 48 ksi, an elongation to failure of 5%, and a shear strength of 25 ksi.

[0058] In still another and/or alternative non-limiting aspect of the invention, there is provided a method for forming a novel magnesium composite including the steps of a) selecting an AZ9ID magnesium alloy having about 9 wt.% aluminum, 1 wt.% zinc and 90 wt.% magnesium, b) melting the AZ9ID magnesium alloy to a temperature above 800°C, c) adding about 10 wt.% copper to the melted AZ9ID magnesium alloy at a temperature that is less than the melting point of copper, d) dispersing the copper in the melted AZ9ID magnesium alloy using chemical mixing agents at a temperature that is less than the melting point of copper, and e) cooling casting the melted mixture in a steel mold. The cast material exhibits a tensile strength of about 14 ksi, an elongation of about 3%, and shear strength of 11 ksi. The cast material dissolves at a rate of about 50 mg/cm^2-hr. in a 3% KCl solution at 90°C. The cast material dissolves at a rate of 0.6

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mg/cm^2-hr. in a 3% KCl solution at 21°C. The cast material can be subjected to an artificial T5 age treatment for about 16 hours at a temperature of 100-200°C. The aged cast material exhibits a tensile strength of 50Ksi, an elongation to failure of 5%, and a shear strength of 25 ksi. The aged cast material dissolved at a rate of 40mg/cm^2-hr in 3% KCI solution at 90°C and 0.5mglcm2-hr in 3% KCI solution at 20°C.

[0059] These and other objects, features and advantages of the present invention will become apparent in light of the following detailed description of preferred embodiments thereof, as illustrated in the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0060] Figs. 1-3 show a typical cast microstructure with galvanically-active *in situ* formed intermetallic phase wetted to the magnesium matrix; and,

[0061] Fig. 4 shows a typical phase diagram to create *in situ* formed particles of an intermetallic $Mg_x(M)$ where M is any element on the periodic table or any compound in a magnesium matrix and wherein M has a melting point that is greater than the melting point of Mg.

DETAILED DESCRIPTION OF THE INVENTION

[0062] The present invention is directed to a novel magnesium composite that can be used to form a castable, moldable, or extrudable component. The magnesium composite includes at least 50 wt.% magnesium. Generally, the magnesium composite includes over 50 wt.% magnesium and less than about 99.5 wt.% magnesium and all values and ranges therebetween. One or more additives are added to a magnesium or magnesium alloy to form the novel magnesium composite of the present invention. The one or more additives can be selected and used in quantities so that galvanically-active intermetallic or insoluble precipitates form in the magnesium or magnesium alloy while the magnesium or magnesium alloy is in a molten state and/or during the cooling of the melt; however, this is not required. The one or more additives are added to the molten magnesium or magnesium alloy at a temperature that is less than the melting point of the one or more additives. During the process of mixing the one or more additives in the molten magnesium or magnesium alloy, the one or more additives are not caused to fully melt in the molten magnesium or magnesium alloy. After the mixing process is completed, the molten magnesium or magnesium alloy and the one or more additives that are mixed in the molten magnesium or

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magnesium alloy are cooled to form a solid component. Such a formation in the melt is called *in situ* particle formation as illustrated in Figs. 1-3. Such a process can be used to achieve a specific galvanic corrosion rate in the entire magnesium composite and/or along the grain boundaries of the magnesium composite. This feature results in the ability to control where the galvanically-active phases are located in the final casting, as well as the surface area ratio of the *in situ* phase to the matrix phase, which enables the use of lower cathode phase loadings as compared to a powder metallurgical or alloyed composite to achieve the same dissolution rates. The *in situ* formed galvanic additives can be used to enhance mechanical properties of the magnesium composite such as ductility, tensile strength, and/or shear strength. The final magnesium composite can also be enhanced by heat treatment as well as deformation processing (such as extrusion, forging, or rolling) to further improve the strength of the final composite over the as-cast material; however, this is not required. The deformation processing can be used to achieve strengthening of the magnesium composite by reducing the grain size of the magnesium composite. Further enhancements, such as traditional alloy heat treatments (such as solutionizing, aging and/or cold working) can be used to enable control of dissolution rates though precipitation of more or less galvanically-active phases within the alloy microstructure while improving mechanical properties; however, this is not required. Because galvanic corrosion is driven by both the electro potential between the anode and cathode phase, as well as the exposed surface area of the two phases, the rate of corrosion can also be controlled through adjustment of the *in situ* formed particles size, while not increasing or decreasing the volume or weight fraction of the addition, and/or by changing the volume/weight fraction without changing the particle size. Achievement of *in situ* particle size control can be achieved by mechanical agitation of the melt, ultrasonic processing of the melt, controlling cooling rates, and/or by performing heat treatments. *In situ* particle size can also or alternatively be modified by secondary processing such as rolling, forging, extrusion and/or other deformation techniques. A smaller particle size can be used to increase the dissolution rate of the magnesium composite. An increase in the weight percent of the *in situ* formed particles or phases in the magnesium composite can also or alternatively be used to increase the dissolution rate of the magnesium composite. A phase diagram for forming *in situ* formed particles or phases in the magnesium composite is illustrated in Fig. 4.

[0063] In accordance with the present invention, a novel magnesium composite is produced by casting a magnesium metal or magnesium alloy with at least one component to form a

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galvanically-active phase with another component in the chemistry that forms a discrete phase that is insoluble at the use temperature of the dissolvable component. The *in situ* formed particles and phases have a different galvanic potential from the remaining magnesium metal or magnesium alloy. The *in situ* formed particles or phases are uniformly dispersed through the matrix metal or metal alloy using techniques such as thixomolding, stir casting, mechanical agitation, chemical agitation, electrowetting, ultrasonic dispersion, and/or combinations of these methods. Due to the particles being formed *in situ* to the melt, such particles generally have excellent wetting to the matrix phase and can be found at grain boundaries or as continuous dendritic phases throughout the component depending on alloy composition and the phase diagram. Because the alloys form galvanic intermetallic particles where the intermetallic phase is insoluble to the matrix at use temperatures, once the material is below the solidus temperature, no further dispersing or size control is necessary in the component. This feature also allows for further grain refinement of the final alloy through traditional deformation processing to increase tensile strength, elongation to failure, and other properties in the alloy system that are not achievable without the use of insoluble particle additions. Because the ratio of *in situ* formed phases in the material is generally constant and the grain boundary to grain surface area is typically consistent even after deformation processing and heat treatment of the composite, the corrosion rate of such composites remains very similar after mechanical processing.

EXAMPLE I

[0064] An AZ91D magnesium alloy having 9 wt.% aluminum, 1 wt.% zinc and 90 wt.% magnesium was melted to above 800°C and at least 200°C below the melting point of nickel. About 7 wt.% of nickel was added to the melt and dispersed. The melt was cast into a steel mold. The cast material exhibited a tensile strength of about 14 ksi, an elongation of about 3%, and shear strength of 11 ksi. The cast material dissolved at a rate of about 75 mg/cm^2-min in a 3% KCl solution at 90°C. The material dissolved at a rate of 1 mg/cm^2-hr in a 3% KCl solution at 21°C. The material dissolved at a rate of 325mg/cm^2-hr. in a 3% KCl solution at 90°C.

EXAMPLE 2

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[0065] The composite in Example 1 was subjected to extrusion with an 11:1 reduction area. The material exhibited a tensile yield strength of 45 ksi, an Ultimate tensile strength of 50 ksi and an elongation to failure of 8%. The material has a dissolve rate of 0.8 mg/cm^2-min. in a 3% KCl solution at 20°C. The material dissolved at a rate of 100 mg/cm^2-hr. in a 3% KCl solution at 90°C.

EXAMPLE 3

[0066] The alloy in Example 2 was subjected to an artificial T5 age treatment of 16 hours from 100°C-200°C. The alloy exhibited a tensile strength of 48 ksi and elongation to failure of 5% and a shear strength of 25 ksi. The material dissolved at a rate of 110 mg/ cm^2-hr. in 3% KCl solution at 90°C and 1 mg/cm^2-hr. in 3% KCl solution at 20°C.

EXAMPLE 4

[0067] The alloy in Example 1 was subjected to a solutionizing treatment T4 of 18 hours from 400°C-500°C and then an artificial T6 aging treatment of 16 hours from 100°C-200C. The alloy exhibited a tensile strength of 34 ksi and elongation to failure of 11% and a shear strength of 18Ksi. The material dissolved at a rate of 84mg/ cm^2-hr. in 3% KCl solution at 90°C and 0.8 mg/cm^2-hr. in 3% KCl solution at 20°C.

EXAMPLE 5

[0068] An AZ91D magnesium alloy having 9 wt.% aluminum, 1 wt.% zinc and 90 wt.% magnesium was melted to above 800°C and at least 200°C below the melting point of copper. About 10 wt.% of copper alloyed to the melt and dispersed. The melt was cast into a steel mold. The cast material exhibited a tensile yield strength of about 14 ksi, an elongation of about 3%, and shear strength of 11 ksi. The cast material dissolved at a rate of about 50 mg/cm^2-hr. in a 3% KCl solution at 90°C. The material dissolved at a rate of 0.6 mg/cm^2-hr. in a 3% KCl solution at 21°C.

EXAMPLE 6

[0069] The alloy in Example 5 was subjected to an artificial T5 aging treatment of 16 hours from 100°C-200°C the alloy exhibited a tensile strength of 50 ksi and elongation to failure of 5%

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and a shear strength of 25 ksi. The material dissolved at a rate of 40 mg/cm^2-hr. in 3% KCl solution at 90°C and 0.5 mg/cm^2-hr. in 3% KCl solution at 20°C.

[0070]   It will thus be seen that the objects set forth above, among those made apparent from the preceding description, are efficiently attained, and since certain changes may be made in the constructions set forth without departing from the spirit and scope of the invention, it is intended that all matter contained in the above description and shown in the accompanying drawings shall be interpreted as illustrative and not in a limiting sense. The invention has been described with reference to preferred and alternate embodiments. Modifications and alterations will become apparent to those skilled in the art upon reading and understanding the detailed discussion of the invention provided herein. This invention is intended to include all such modifications and alterations insofar as they come within the scope of the present invention. It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described and all statements of the scope of the invention, which, as a matter of language, might be said to fall there between. The invention has been described with reference to the preferred embodiments. These and other modifications of the preferred embodiments as well as other embodiments of the invention will be obvious from the disclosure herein, whereby the foregoing descriptive matter is to be interpreted merely as illustrative of the invention and not as a limitation. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims.

What is claimed:

1.   A method of controlling the dissolution properties of a magnesium or a magnesium alloy comprising of the steps of:

heating the   magnesium or a magnesium alloy to a point above its solidus temperature;

adding an additive material to said magnesium or magnesium alloy while said magnesium or magnesium alloy is above said solidus temperature of magnesium or magnesium alloy to form a mixture, said additive material having a greater melting point temperature than said solidus temperature of said magnesium or magnesium alloy, said additive material constituting about 0.05 wt %-45 wt % of said mixture;

dispersing said additive material in said mixture while said magnesium or magnesium alloy is above said solidus temperature of magnesium or magnesium alloy; and,

cooling said mixture to form a said magnesium composite, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases.

2.   The method as defined in claim 1, including the step of controlling a size of said in situ precipitated intermetallic phase by controlled selection of a mixing technique during said dispersion step, controlling a cooling rate of said mixture, or combinations thereof.

3.   The method as defined in claim 1, wherein said magnesium or magnesium alloy is heated to a temperature that is less than said melting point temperature of said additive material.

4.   The method as defined in claim 2, wherein said magnesium or magnesium alloy is heated to a temperature that is less than said melting point temperature of said additive material.

5.   The method as defined in claim 1, wherein said additive includes one or more metals selected from the group consisting of copper, silicon, nickel and cobalt.

6.   The method as defined in claim 4, wherein said additive includes one or more metals selected from the group consisting of copper, silicon, nickel and cobalt.

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7.　　The method as defined in claim 1, wherein said additive is formed of a single composition, and have an average particle diameter size of about 0.1-500 microns.

8.　　The method as defined in claim 6, wherein said additive is formed of a single composition, and have an average particle diameter size of about 0.1-500 microns.

9.　　The method as defined in claim 1, wherein said magnesium alloy includes over 50 wt % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

10.　　The method as defined in claim 9, wherein said magnesium alloy includes over 50 wt % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt %, zinc in amount of about 0.1-6 wt %, zirconium in an amount of about 0.01-3 wt %, manganese in an amount of about 0.15-2 wt %; boron in amount of about 0.0002-0.04 wt %, and bismuth in amount of about 0.4-0.7 wt %.

11.　　The method as defined in claim 8, wherein said magnesium alloy includes over 50 wt % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt %, zinc in amount of about 0.1-3 wt %, zirconium in an amount of about 0.01-1 wt %, manganese in an amount of about 0.15-2 wt %; boron in amount of about 0.0002-0.04 wt %, and bismuth in amount of about 0.4-0.7 wt %.

12.　　The method as defined in claim 1, including the step of solutionizing said magnesium composite at a temperature above 300°C and below a melting temperature of said magnesium composite to improve tensile strength, ductility, or combinations thereof of said magnesium composite.

13.　　The method as defined in claim 11, including the step of solutionizing said magnesium composite at a temperature above 300°C and below a melting temperature of said magnesium composite to improve tensile strength, ductility, or combinations thereof

of said magnesium composite.

14.   The method as defined in claim 1, including the step of aging said magnesium composite at a temperature of above 100°C and below 300°C to improve tensile strength of said magnesium composite.

15.   The method as defined in claim 13, including the step of aging said magnesium composite at a temperature of above 100°C and below 300°C to improve tensile strength of said magnesium composite.

16.   The method as defined in claim 1, wherein said additive metal includes about 0.05-35 wt % nickel, said nickel forms intermetallic Mg_xNi as a galvanically-active in situ precipitate in said magnesium composite.

17.   The method as defined in claim 15, wherein said additive metal includes about 0.05-35 wt % nickel, said nickel forms intermetallic Mg_xNi as a galvanically-active in situ precipitate in said magnesium composite.

18.   The method as defined in claim 1, wherein said additive includes about 0.05-35 wt % copper, said copper forms intermetallic $CuMg_x$ as the galvanically-active in situ precipitate in said magnesium composite.

19.   The method as defined in claim 15, wherein said additive includes about 0.05-35 wt % copper, said copper forms intermetallic $CuMg_x$ as the galvanically-active in situ precipitate in said magnesium composite.

20.   The method as defined in claim 1, wherein said additive includes about 0.05-35 wt % cobalt, said cobalt forms intermetallic $CoMg_x$ as the galvanically-active in situ precipitate in said magnesium composite.

21. The method as defined in claim 15, wherein said additive includes about 0.05-35 wt % cobalt, said cobalt forms intermetallic $CoMg_x$ as the galvanically-active in situ precipitate in said magnesium composite.

22. A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases comprising a magnesium or a magnesium alloy, an additive material having a greater melting point temperature than a solidus temperature of said magnesium or magnesium alloy, said additive material constituting about 0.05 wt %-45 wt % of said mixture, said additive material forming metal composite particles or precipitant in said magnesium composite that include said additive material and magnesium, said metal composite particles or precipitant forming said in situ precipitation of said galvanically-active intermetallic phases.

23. The magnesium composite as defined in claim 22, wherein said additive includes one or more metals selected from the group consisting of copper, silicon, nickel and cobalt.

24. The magnesium composite as defined in claim 22, wherein said magnesium alloy includes over 50 wt % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

25. The magnesium composite as defined in claim 22, wherein said magnesium alloy includes over 50 wt % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt %, zinc in amount of about 0.1-3 wt %, zirconium in an amount of about 0.01-1 wt %, manganese in an amount of about 0.15-2 wt %, boron in amount of about 0.0002-0.04 wt %, and bismuth in amount of about 0.4-0.7 wt %.

26. The magnesium composite as defined in claim 22, wherein said additive metal includes about 0.05-35 wt % nickel, said nickel forms intermetallic Mg_xNi as a galvanically-active in situ precipitate in said magnesium composite.

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27. The magnesium composite as defined in claim 22, wherein said additive includes about 0.05-35 wt % copper, said copper forms intermetallic $CuMg_x$ as the galvanically-active in situ precipitate in said magnesium composite.

28. The magnesium composite as defined in claim 22, wherein said additive includes about 0.05-35 wt % cobalt, said cobalt forms intermetallic $CoMg_x$ as the galvanically-active in situ precipitate in said magnesium composite.

29. The magnesium composite as defined in claim 22, where the use of a deformation processing such as forging or extrusion is used to reduce grain size of said magnesium composite, increase tensile yield strength of said magnesium composite, increase elongation of said magnesium composite, or combinations thereof.

30. The magnesium composite as defined in claim 22, wherein said magnesium composite is subjected to a surface treatment to improve a surface hardness of said magnesium composite, said surface treatment including peening, heat treatment, aluminizing, or combinations thereof.

31. The magnesium composite as defined in claim 22, wherein a dissolution rate of said magnesium composite is about 5-300 mg/cm2/hr in 3 wt % KCl water mixture at 90° C.

32. The magnesium composite as defined in claim 22, wherein a dissolution rate of said magnesium composite is controlled by an amount and size of said in situ formed galvanically-active particles whereby smaller average sized particles of said in situ formed galvanically-active particles, a greater weight percent of said in situ formed galvanically-active particles in said magnesium composite, or combinations thereof increases said dissolution rate of said magnesium composite.

ABSTRACT OF THE DISCLOSURE

A castable, moldable, and/or extrudable structure using a metallic primary alloy. One or more additives are added to the metallic primary alloy so that *in situ* galvanically-active reinforcement particles are formed in the melt or on cooling from the melt. The composite contain an optimal composition and morphology to achieve a specific galvanic corrosion rate in the entire composite. The *in situ* formed galvanically-active particles can be used to enhance mechanical properties of the composite, such as ductility and/or tensile strength. The final casting can also be enhanced by heat treatment, as well as deformation processing such as extrusion, forging, or rolling, to further improve the strength of the final composite over the as-cast material.

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Magnesium composite Matrix (1)

In situ Formed Particles (2)

50um

FIG 1.

In situ formed particles

Matrix magnesium
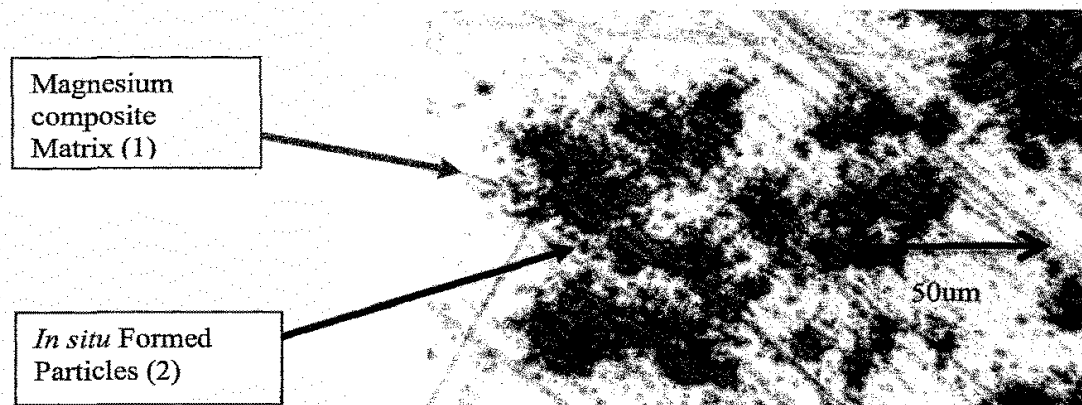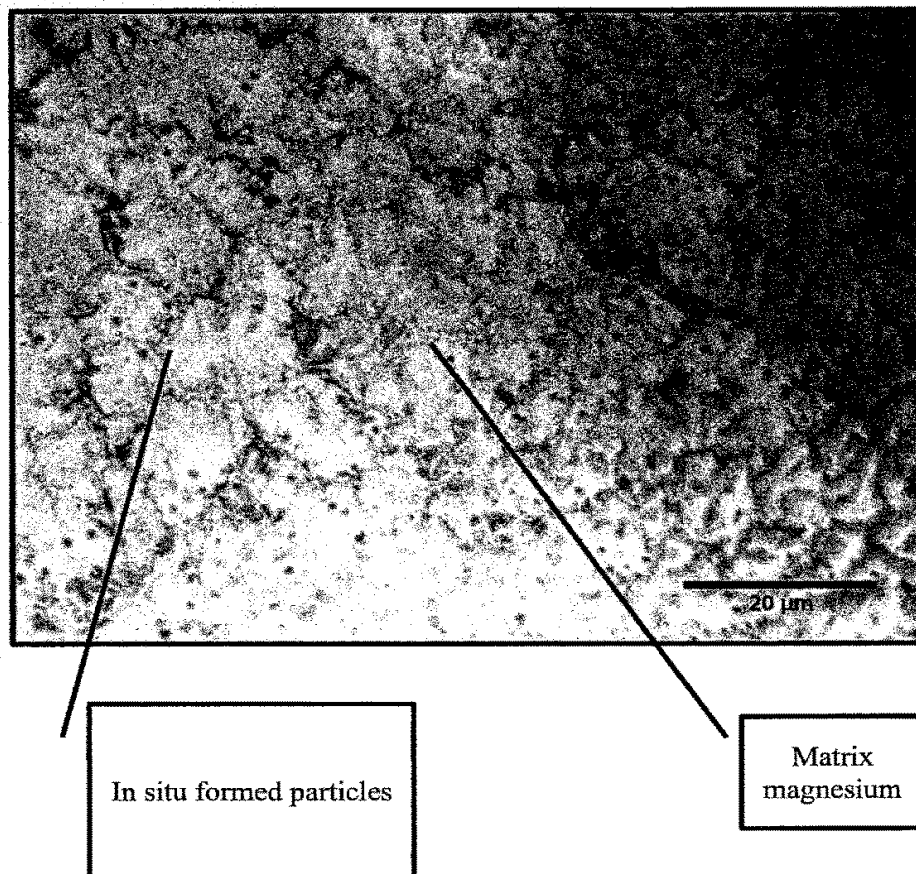
FIG. 2
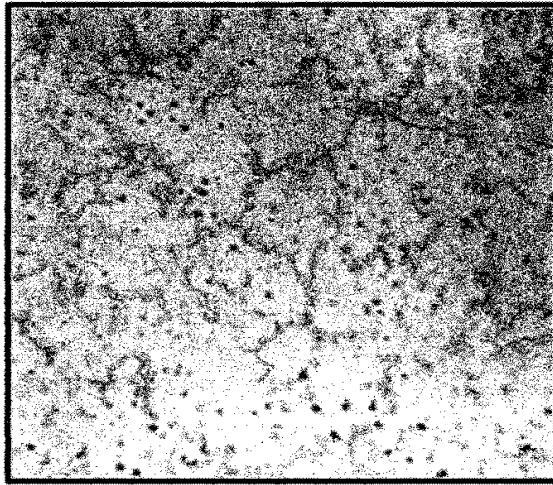
Highlighted In Situ Formed Particles

FIG. 3
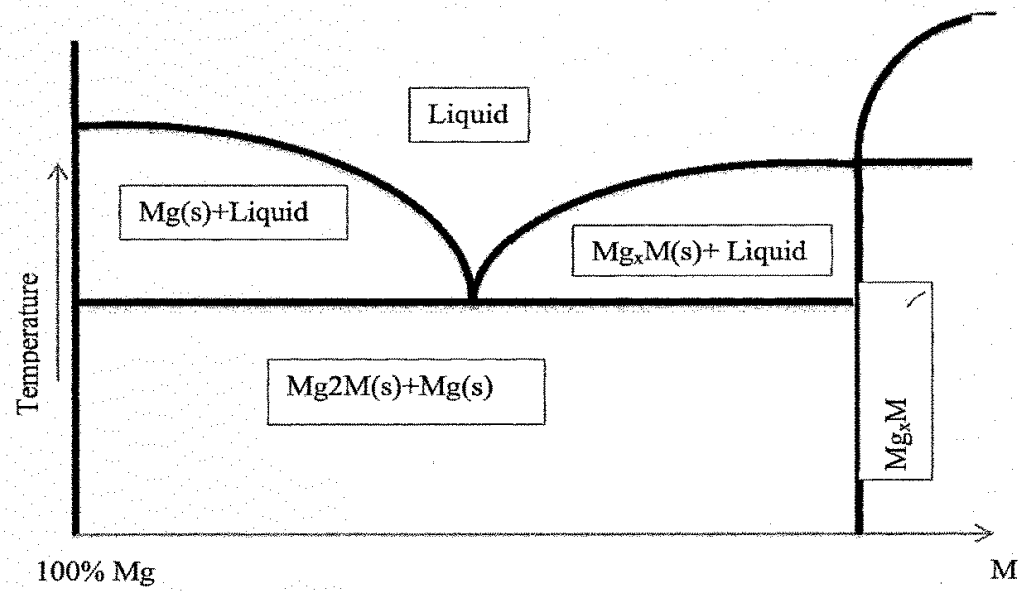
FIG. 4

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	:	Brian P. Doud et al.
For	:	GALVANICALLY-ACTIVE IN SITU FORMED PARTICLES FOR CONTROLLED RATE DISSOLVING TOOLS
Our Docket	:	POWD 2 00033 US02

PRELIMINARY AMENDMENT

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

Dear Sir:

Please amend the above-identified patent application as follows:

IN THE CLAIMS:

Claims 1-21 (Canceled).

22.   (Currently Amended) A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite comprising a magnesium or a magnesium alloy, an additive material having a greater melting point temperature than a solidus temperature of said magnesium or magnesium alloy, said additive material constituting about 0.05 wt.% - 45 wt.% of said mixture, said additive material forming metal composite particles or precipitant in said magnesium composite that include said additive material and magnesium, said metal composite particles or precipitant forming said in situ precipitation of said galvanically-active intermetallic phases.

23.   (Currently Amended) The magnesium composite as defined in claim 22, wherein said additive includes one or more metals selected from the group consisting of copper, silicon, nickel, titanium, iron, and cobalt.

24.   (Currently Amended) The magnesium composite as defined in claim 22, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum, boron, bismuth, zinc, zirconium, and manganese.

25.   (Currently Amended) The magnesium composite as defined in claim 22, wherein said magnesium alloy includes over 50 wt.% magnesium and one or more metals selected from the group

consisting of aluminum in an amount of about 0.5-10 wt.%, zinc in amount of about 0.1-3 wt.%, zirconium in an amount of about 0.01-1 wt.%, manganese in an amount of about 0.15-2 wt.%, boron in amount of about 0.0002-0.04 wt.%, and bismuth in amount of about 0.4-0.7 wt.%.

26.   (Currently Amended) The magnesium composite as defined in claim 22, wherein said additive metal includes about 0.05-35 wt.% nickel, said nickel forms intermetallic Mg_xNi as a galvanically-active in situ precipitate in said magnesium composite.

27.   (Currently Amended) The magnesium composite as defined in claim 22, wherein said additive includes about 0.05-35 wt.% copper, said copper forms intermetallic $CuMg_x$ as the galvanically-active in situ precipitate in said magnesium composite.

28.   (Currently Amended) The magnesium composite as defined in claim 22, wherein said additive includes about 0.05-35 wt.% cobalt, said cobalt forms intermetallic $CoMg_x$ as the galvanically-active in situ precipitate in said magnesium composite.

29.   (Original) The magnesium composite as defined in claim 22, where the use of a deformation processing such as forging or extrusion is used to reduce grain size of said magnesium composite, increase tensile yield strength of said magnesium composite, increase elongation of said magnesium composite, or combinations thereof.

30. (Original) The magnesium composite as defined in claim 22, wherein said magnesium composite is subjected to a surface treatment to improve a surface hardness of said magnesium composite, said surface treatment including peening, heat treatment, aluminizing, or combinations thereof.

31. (Currently Amended) The magnesium composite as defined in claim 22, wherein a dissolution rate of said magnesium composite is about 5-~~300~~325 mg/cm2/hr in 3 wt. % KCl water mixture at 90°C.

32. (Original) The magnesium composite as defined in claim 22, wherein a dissolution rate of said magnesium composite is controlled by an amount and size of said in situ formed galvanically-active particles whereby smaller average sized particles of said in situ formed galvanically-active particles, a greater weight percent of said in situ formed galvanically-active particles in said magnesium composite, or combinations thereof increases said dissolution rate of said magnesium composite.

33. (New) A magnesium composite that includes in situ precipitation of galvanically-active intermetallic phases to enable controlled dissolution of said magnesium composite comprising a magnesium or a magnesium alloy, an additive material having a greater melting point temperature than a solidus temperature of said magnesium or magnesium alloy, said composite including greater than 50 wt.% magnesium, said additive material constituting about 0.05-45 wt.% of said magnesium composite, said additive material having a melting point temperature

that is greater than 100°C than a melting temperature of said magnesium or magnesium alloy, an average particle diameter size of said additive material is at least 0.1 microns and up to about 500 microns, said additive including one or more metals selected from the group consisting of copper, nickel, cobalt, titanium, silicon, and iron, a portion of said additive material forming solid particles with said magnesium and a portion of said additive material remaining unalloyed additive material, said magnesium composite including in situ precipitation of galvanically-active intermetallic phases that includes said unalloyed additive material and said solid particles formed of magnesium additive material.

34. (New) The magnesium composite as defined in claim 33, wherein said additive material is added to said magnesium or magnesium alloy while said magnesium or magnesium alloy is at a temperature that is above said solidus temperature of magnesium or magnesium alloy and a temperature that is less than a melting point of said additive material to form a mixture.

35. (New) The magnesium composite as defined in claim 33, wherein said magnesium alloy includes over 50 wt. % magnesium and one or more metals selected from the group consisting of aluminum in an amount of about 0.5-10 wt %, zinc in amount of about 0.1-6 wt. %, zirconium in an amount of about 0.01-3 wt. %, manganese in an amount of about 0.15-2 wt. %; boron in amount of about 0.0002-0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %.

36. (New) The magnesium composite as defined in claim 34, wherein said magnesium alloy includes over 50 wt % magnesium and one or more metals selected from the group consisting

of aluminum in an amount of about 0.5-10 wt. %, zinc in amount of about 0.1-3 wt. %, zirconium in an amount of about 0.01-1 wt. %, manganese in an amount of about 0.15-2 wt. %; boron in amount of about 0.0002-0.04 wt. %, and bismuth in amount of about 0.4-0.7 wt. %.

37.　　(New) The magnesium composite as defined in claim 33, said additive metal includes about 0.05-35 wt.% nickel, said nickel forms intermetallic Mg_xNi as a galvanically-active in situ precipitate in said magnesium composite.

38.　　(New) The magnesium composite as defined in claim 36, wherein said additive metal includes about 0.05-35 wt.% nickel, said nickel forms intermetallic Mg_xNi as a galvanically-active in situ precipitate in said magnesium composite.

39.　　(New) The magnesium composite as defined in claim 37, wherein said additive metal includes about 3-7 wt.% nickel.

40.　　(New) The magnesium composite as defined in claim 38, wherein said additive metal includes about 7-10 wt.% nickel.

41.　　(New) The magnesium composite as defined in claim 37, wherein said additive metal includes about 3-7 wt.% nickel.

42.   (New) The magnesium composite as defined in claim 38, wherein said additive metal includes about 7-10 wt.% nickel.

43.   (New) The magnesium composite as defined in claim 33, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm^2/hr in 3 wt.% KCl water mixture at 90°C and up to 325 mg/cm^2/hr in 3 wt.% KCl water mixture at 90°C.

44.   (New) The magnesium composite as defined in claim 38, wherein a dissolution rate of said magnesium composite is at least 45 mg/cm^2/hr in 3 wt.% KCl water mixture at 90°C and up to 325 mg/cm^2/hr in 3 wt.% KCl water mixture at 90°C.

REMARKS

Applicant has, by this Amendment, canceled claim 1-21, amended claims 22-28, and 31, and added new claims 33-44.
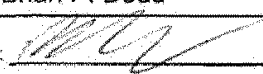
Applicant submits that the claims pending in the above-identified patent application are in allowable form.

Respectfully submitted,
FAY SHARPE LLP

By:

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DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	Galvanically-Active In Situ Formed Particles For Controlled Rate Dissolving Tools

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☑ United States application or PCT international application number __14/689,295__

filed on __April 17, 2015__ .

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

LEGAL NAME OF INVENTOR

Inventor: __Brian P. Doud__   Date (Optional): __4-20-15__

Signature: _____

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	Galvanically-Active In Situ Formed Particles For Controlled Rate Dissolving Tools

As the below named inventor, I hereby declare that:

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I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

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LEGAL NAME OF INVENTOR

Inventor: **Nicholas J. Farkas**   Date (Optional) : **4/20/15**

Signature: *[signature]*

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

DECLARATION (37 CFR 1.63) FOR UTILITY OR DESIGN APPLICATION USING AN APPLICATION DATA SHEET (37 CFR 1.76)

Title of Invention	Galvanically-Active In Situ Formed Particles For Controlled Rate Dissolving Tools

As the below named inventor, I hereby declare that:

This declaration is directed to:

☐ The attached application, or

☑ United States application or PCT international application number 14/689,295

filed on April 17, 2015

The above-identified application was made or authorized to be made by me.

I believe that I am the original inventor or an original joint inventor of a claimed invention in the application.

I hereby acknowledge that any willful false statement made in this declaration is punishable under 18 U.S.C. 1001 by fine or imprisonment of not more than five (5) years, or both.

WARNING:

Petitioner/applicant is cautioned to avoid submitting personal information in documents filed in a patent application that may contribute to identity theft. Personal information such as social security numbers, bank account numbers, or credit card numbers (other than a check or credit card authorization form PTO-2038 submitted for payment purposes) is never required by the USPTO to support a petition or an application. If this type of personal information is included in documents submitted to the USPTO, petitioners/applicants should consider redacting such personal information from the documents before submitting them to the USPTO. Petitioner/applicant is advised that the record of a patent application is available to the public after publication of the application (unless a non-publication request in compliance with 37 CFR 1.213(a) is made in the application) or issuance of a patent. Furthermore, the record from an abandoned application may also be available to the public if the application is referenced in a published application or an issued patent (see 37 CFR 1.14). Checks and credit card authorization forms PTO-2038 submitted for payment purposes are not retained in the application file and therefore are not publicly available.

LEGAL NAME OF INVENTOR

Inventor: Andrew J. Sherman

Date (Optional): 4/17/11

Signature:

Note: An application data sheet (PTO/SB/14 or equivalent), including naming the entire inventive entity, must accompany this form or must have been previously filed. Use an additional PTO/AIA/01 form for each additional inventor.

Electronic Patent Application Fee Transmittal

Application Number:	
Filing Date:	
Title of Invention:	GALVANICALLY-ACTIVE IN SITU FORMED PARTICLES FOR CONTROLLED RATE DISSOLVING TOOLS
First Named Inventor/Applicant Name:	Brian P. Doud
Filer:	Brian Erkin Turung/mel rohan
Attorney Docket Number:	POWD 200033US02

Filed as Small Entity

Filing Fees for   Utility under 35 USC 111(a)

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Basic Filing:				
UTILITY FILING FEE (ELECTRONIC FILING)	4011	1	70	70
UTILITY SEARCH FEE	2111	1	300	300
UTILITY EXAMINATION FEE	2311	1	360	360
Pages:				
Claims:				
CLAIMS IN EXCESS OF 20	2202	3	40	120
Miscellaneous-Filing:				
Petition:				

Description	Fee Code	Quantity	Amount	Sub-Total in USD($)
Patent-Appeals-and-Interference:				
Post-Allowance-and-Post-Issuance:				
Extension-of-Time:				
Miscellaneous:				
		Total in USD ($)		850

Electronic Acknowledgement Receipt

EFS ID:	29685698
Application Number:	15641439
International Application Number:	
Confirmation Number:	2533
Title of Invention:	GALVANICALLY-ACTIVE IN SITU FORMED PARTICLES FOR CONTROLLED RATE DISSOLVING TOOLS
First Named Inventor/Applicant Name:	Brian P. Doud
Customer Number:	27885
Filer:	Brian Erkin Turung/mel rohan
Filer Authorized By:	Brian Erkin Turung
Attorney Docket Number:	POWD 200033US02
Receipt Date:	05-JUL-2017
Filing Date:	
Time Stamp:	11:34:23
Application Type:	Utility under 35 USC 111(a)

Payment information:

Submitted with Payment	yes
Payment Type	CARD
Payment was successfully received in RAM	$850
RAM confirmation Number	070517INTEFSW11351500
Deposit Account	060308
Authorized User	Brian Turung
The Director of the USPTO is hereby authorized to charge indicated fees and credit any overpayment as follows:	
37 CFR 1.16 (National application filing, search, and examination fees)	
37 CFR 1.21 (Miscellaneous fees and charges)	

File Listing:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
1	Transmittal of New Application	DivisionalTransmittal.pdf	161167 e8fb143de5ffd131d85ae8add6a1a75d216 84e67	no	3

Warnings:

Information:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
2	Application Data Sheet	ADS.pdf	1576162 86b6ba822bebf4c0e6121bf84a906015107 8b914	no	7

Warnings:

Information:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
3		DivisionalApplication.pdf	4624018 aa427a8b02739b3e8ab7f76ba949dd213aa a399a	yes	35

Multipart Description/PDF files in .zip description		
Document Description	Start	End
Specification	1	25
Claims	26	30
Abstract	31	31
Drawings-other than black and white line drawings	32	35

Warnings:

Information:

Document Number	Document Description	File Name	File Size(Bytes)/ Message Digest	Multi Part /.zip	Pages (if appl.)
4		PreliminaryAmendment.pdf	484518 6b0139ae8a67abf2ae8c6a9ba32fef83dc76 a927	yes	8

Multipart Description/PDF files in .zip description		
Document Description	Start	End

Preliminary Amendment		1	1
Claims		2	7
Applicant Arguments/Remarks Made in an Amendment		8	8

Warnings:

Information:

5	Oath or Declaration filed	ExecutedDeclarations.pdf	538718 f735567b5698abaf287103bcfe08a17e3647c541	no	3

Warnings:

Information:

6	Fee Worksheet (SB06)	fee-info.pdf	36781 b8fc145fa60f2b026675df19d307e487a0cce754	no	2

Warnings:

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Total Files Size (in bytes):	7421364

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If a new application is being filed and the application includes the necessary components for a filing date (see 37 CFR 1.53(b)-(d) and MPEP 506), a Filing Receipt (37 CFR 1.54) will be issued in due course and the date shown on this Acknowledgement Receipt will establish the filing date of the application.
National Stage of an International Application under 35 U.S.C. 371
If a timely submission to enter the national stage of an international application is compliant with the conditions of 35 U.S.C. 371 and other applicable requirements a Form PCT/DO/EO/903 indicating acceptance of the application as a national stage submission under 35 U.S.C. 371 will be issued in addition to the Filing Receipt, in due course.
New International Application Filed with the USPTO as a Receiving Office
If a new international application is being filed and the international application includes the necessary components for an international filing date (see PCT Article 11 and MPEP 1810), a Notification of the International Application Number and of the International Filing Date (Form PCT/RO/105) will be issued in due course, subject to prescriptions concerning national security, and the date shown on this Acknowledgement Receipt will establish the international filing date of the application.

SCORE Placeholder Sheet for IFW Content

Application Number: 15641439   Document Date: 07/05/2017

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Form Revision Date: August 26, 2013